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HIGH TEMPERATURE RESINS FOR COMPOSITES

Acurex Corporation/Aerotherm Division
485 Clyde Avenue
Mountain View, California 94042

November 1977

TECHNICAL REPORT AFML-TR-77-188

Final Report for the Period 28 June 1976 — 15 June 1977

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
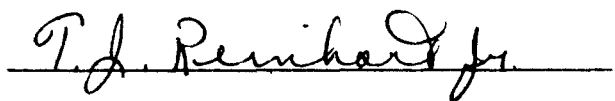WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This technical report has been reviewed and is approved for publication.

T. APONYI
Project Monitor

FOR THE COMMANDER

T. J. REINHART, JR., Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Three Air Force resin systems were investigated for their potential to achieve their individual merits in graphite composites. The three resins were Thermid 600, acetylene-terminated quinoxalines (ATQ), and polyimidazoquinazoline (PIQ). Hot-melt prepreg techniques were investigated and found to give higher quality prepregs (lower volatile content) than solution techniques for the Thermid 600. High quality composites were produced from prepregs produced by both methods. The ATQ oligomer was synthesized, solution prepregged, and then processed into graphite

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composites. PIQ was synthesized and hot-melt prepregged, and did not pro-
duce a high quality laminate. This is probably due to fiber or fiber-
finish instability at the high cure temperatures required. Celion 3000
was selected from thermal oxidative tests carried out on several fibers
at 700°F.

FOREWORD

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SECTION 1

PROGRAM HIGHLIGHTS AND SUMMARY

Aerotherm is investigating three resin systems developed by the Air Force for use in graphite composites. They are the acetylene-terminated polyimide (Thermid 600), acetylene-terminated quinoxalines (ATQ), and polyimidazoquinazolines (PIQ). This report covers the first 12 months of a 21-month technical effort.

Since all three resins are solids at room temperature, the graphite prepregs will necessarily be tack free. This type of prepreg is not unfamiliar; in fact, Aerotherm fabricated a full-sized PBI/glass fabric radome from such a prepreg a few years ago. Some innovative layup and processing techniques require development, but the easy processing features of the addition cured acetylene-teminated polyimides and quinoxalines more than offset the minor handling deficiencies of a no-tack prepreg.

We have demonstrated the preparation of high-quality Thermid 600 graphite composites from both solution and hot-melt prepregs. The merits of the successful hot-melt approach to Thermid 600 graphite prepregs far outweigh the disadvantage (standard hot-melt equipment cannot be used). Prepregs with typically less than 1-percent volatiles were invariably obtained by using hot-melt methods. Also, since Thermid 600 has a low volatile content and rapid gel properties, a high-quality graphite composite is virtually assured by either in-hot at $252^\circ C$ ($485^\circ F$) match-die molding techniques or rapid heat rise ($14^\circ F$/minute) autoclave techniques.

Thermid 600, as produced by Gulf Oil Chemical Company, was found acceptable on a batch-to-batch basis as a raw material for high-quality prepregs, with the exception of residual volatiles and variable low-temperature flow properties. The residual volatiles, averaging about 2 percent, cause some foaming in the hot-melt prepregging operation when conducted at temperatures in excess of $550^\circ F$. Batch-to-batch variation of Thermid 600 performance in aging at $600^\circ F$ or $700^\circ F$ was not tested.

From these initial efforts, the future of Thermid 600 seems assured, even though the minimal flow and gel properties limit processing. Successful efforts to increase either the flow or gel time characteristics of Thermid 600 should provide prepregs which can be processed in any autoclave.

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An important discovery directly related to Thermid 600 prepreg quality and processing was made early in the program. The as-received Thermid 600 possesses some microcrystallinity. This is discernible by DSC and, under certain conditions, by visual examination. When Thermid 600 is processed briefly at high temperatures, the crystallinity is removed. A clear resin is produced which is more easily processed than the as-received Thermid 600.

The ATQ polymers were found to possess flow and gel properties similar to Thermid 600. ATQ graphite composite properties equal to those reported by the AFML, were repeated by our laboratories. The most promising syntheses of a low-cost ATQ structure have been identified and are now being developed.

Polyimidazoquinazoline (PIQ) remains a most attractive resin matrix for use in graphite composites at very high temperatures. Earlier Aerotherm efforts were carried out with Modmor II fibers, which were the best available at that time. Celion 3000, a most promising new fiber, was used with Thermid 600 but did not provide the quality graphite composite we wanted with PIQ. The need for better resin fiber wetting and various fiber surface treatments was indicated.

The PIQ resin was successfully hot-melt prepregged.

SECTION 2

TECHNICAL DISCUSSION

2.1 INTRODUCTION

Several new resin systems have been developed as a result of Air Force requirements for improved graphite, quartz, or glass composites. The subject of this program is to develop processing methods for three of these resin systems, and more specifically develop graphite prepregs from these resin systems.

The three resin systems are being investigated for their potential to provide improved graphite composites. These resin systems are acetylene-terminated polyimides, acetylene-terminated quinoxalines, and polyimidazo-quinazolines. The merits of the three systems and the reasons for selecting them for this effort are summarized below:

- Acetylene-terminated polyimides (Thermid 600) -- no volatile release upon cure; performance capability to at least 600°F

- Acetylene-terminated quinoxalines (ATQ) -- no volatile release upon cure; more soluble than the polyimides, and more easily processed; performance temperatures of at least 450°F are indicated

- Polyimidazoquinazolines (PIQ) -- volatiles released upon cure, but performance temperatures up to at least 900°F have been demonstrated

The following discussion details our progress during the first 12 months of the program. It is divided into three sections, each of which describes efforts on one of the three resin systems. A fourth section documents effort conducted on low-cost approaches to ATQ.

2.2 THERMID 600 DEVELOPMENT

This addition-cured resin system, originally developed for the Air Force by Hughes Aircraft Company as HR-600, is presently being offered by Gulf Oil Chemical Company under the trade name of Thermid 600. It is currently made in less than 50-pound lots, but large-scale manufacture is scheduled sometime in the future.

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The first 12 months of this program focused on selecting the most suitable graphite reinforcement for Thermid 600, identifying prepregging methods suitable for the experienced variations in the raw materials, determining prepreg quality, and fabricating and testing graphite composites.

2.2.1 Reinforcement Selection

Two basic criteria were established for the reinforcement to be used with Thermid 600:

- Thermal-oxidative stability at 550°F and 700°F

- Suitability for use with Thermid 600 to provide a usable prepreg, i.e., fiber compatibility and prepreg production in unidirectional versus woven forms

As discussed below, two reinforcements were used in early Thermid 600 efforts. These reinforcements were Thornel 300 and Celion 3000.

A broad range of graphite fibers was evaluated for thermal oxidative stability. This section describes the results of those fiber tests, with the exception of Celion.

Celanese's Celion 3000 fiber series was announced during the first year of this program. In initial tests this fiber provided thermal oxidative stability nearly equivalent to GY-70 (discussed later). Complete thermal oxidative stability and Thermid 600 composite evaluations with Celion 3000 are in progress.

Preliminary information on the Celion 3000 fiber is provided in Section 2.5.1. This fiber's combination of properties (thermal oxidative resistance, strength, and modulus) appears most promising, and it has been selected for use with Thermid 600 in the second year's effort.

Thermal Oxidative Testing

The 550°F and 700°F fiber air stability test series were conducted under isothermal conditions. All fibers had polyacrylonitrile (PAN) precursors. The test matrix for this series is shown in Table 1. Table 1 also provides typical properties of these fibers. Fibers were included to provide a range of both modulus and strength.

As shown in Figure 1, at 550°F, the Modmor II (surface treated) and Hercules HM/PVA fibers had the lowest weight change. The AS-1 and HT-S fibers had the highest weight loss.

At 700°F, the AS-1 and HT-S fibers were consumed after 125 hours. Thornel 300, with both UC 307 and UC 309 epoxy-compatible sizings, lost approximately 100 percent of its original weight after 150 hours exposure. These data are shown in Figure 2. Both the HM/PVA and surface-treated GY-70 (single end) had less than a 5-percent weight loss at 700°F after 250 hours.

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TABLE 1. ISOTHERMAL AIR AGING SERIES 1 TEST MATRIX

Fiber Identity	Grade	Surface Condition	Filaments per Yarn	Young's Modulus 10^3 (psi)	Tensile Ultimate 10^6 (psi)	Aging Temperature (°F)	
						550	700
Thornel 300	WYP30-I/O	UC 307	10,000	34	360	X	X
Thornel 300	WYP30-I/O	UC 309	3,000	34	360	X	X
Thornel 300	WYP15-I/O	UC 314	6,000	34	360	X	
AS-1	--	Surface Treated	10,000	32-34	410	X	X
HT-S	--	Surface Treated	10,000	34-37	400	X	X
HM	--	PVA[a]	3,000	55	350	X	X
GY-70	Single End	Surface Treated	384	77	250	X	X
Modmor	Type II	Surface Treated	10,000	40	375	X	

[a]Not surface treated

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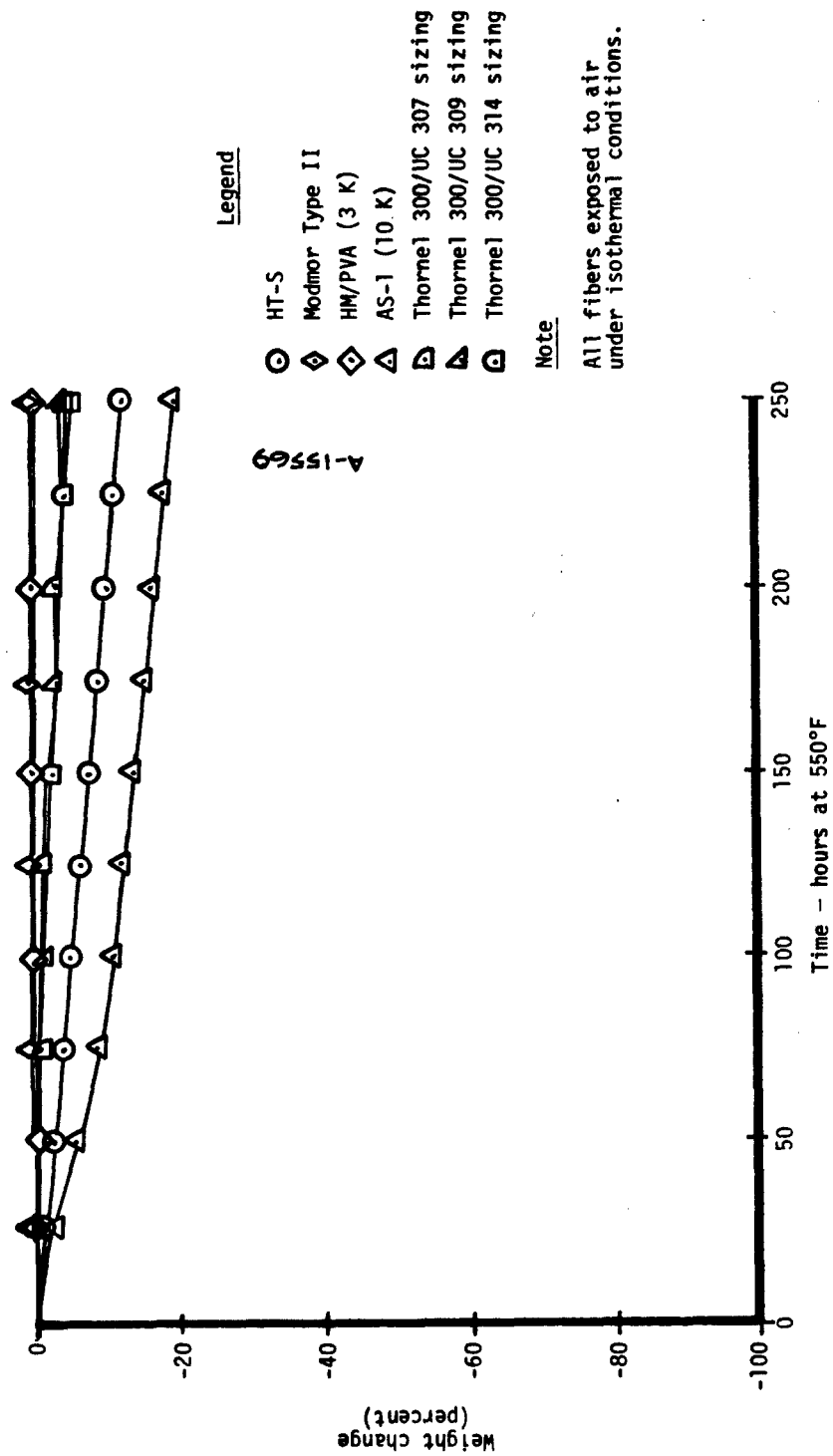
Figure 1. 550°F fiber thermal oxidative stability results.
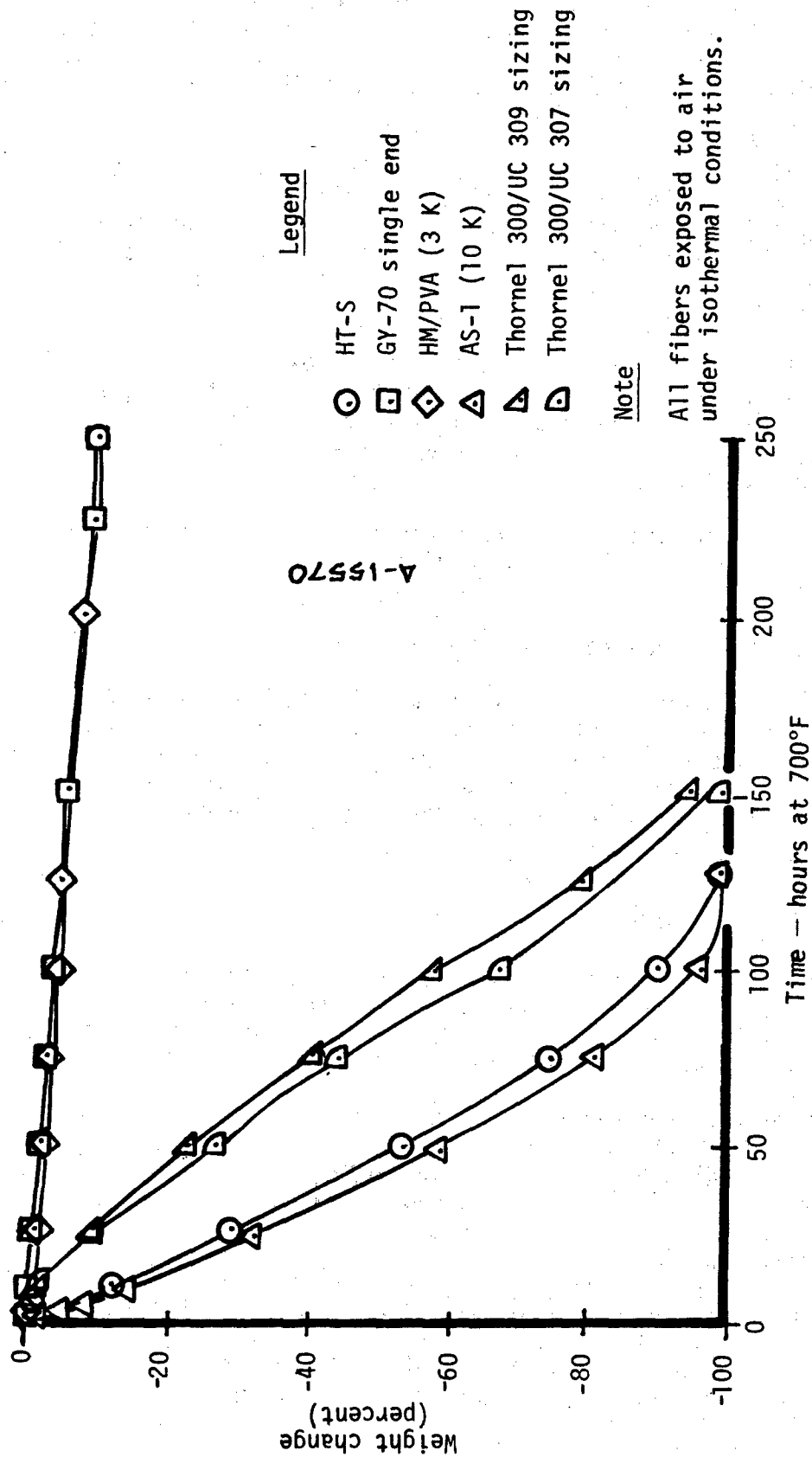
Figure 2. 700°F fiber thermal oxidative stability results.

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The initial weight loss for each fiber through 100 hours is shown in Figures 3 and 4. At 550°F, both the AS-1 and HT-S fibers began losing significant weight after 3 hours. At 700°F, these fibers begin losing weight upon initial exposures. For Thornel 300 fibers, the time for initial significant weight loss decreased from approximately 100 hours to 10 hours with temperature increase from 550°F to 700°F.

Modifying the Thornel 300 surface condition can result in significantly improved thermal oxidative performance. The higher fiber weight loss with increased temperature was noted in the preceding paragraph. A surface-modified Thornel 300, in a 600°F air environment, retained an equivalent amount of weight as an unmodified Thornel 300 in a 550°F air environment (Reference 1).

This data is presented in Figure 5. As shown, the Thornel 300 yarn with UC 307 sizing lost approximately 4 percent of its starting weight after 200 hours at 550°F. Four-percent weight loss after 200 hours at 600°F was obtained with modified fiber surfaces (Reference 1). These conditions are also listed in Figure 5.

A summary of manufacturers' reported data on the specific fiber batches procured for this effort is provided in Table 2.

2.2.2 Thermid 600 Procurement Characterization

Aerotherm received a total of seven separate batches of Thermid 600 during the first year's effort. These batches include resin powder from five Gulf production runs and two additional batches of resin removed at selected processing points in one production run. Batch identities and their history are summarized in Table 3. Prepolymer characterization data are discussed below.

Prepolymer Characterization

A standard characterization test series was established for Thermid 600 resin. This test series was conducted to fully define the various oligomer batches to be used in prepregs and composites. The polymer quality level was established, and basic data was obtained to evaluate processing.

Data from the as-received Thermid 600 characterization tests are reported in Table 4. Characterization data from tests on Thermid 600 from which the residual NMP solvent was removed from the as-received Thermid 600 are also summarized in Table 4 and discussed below.

The first experiments were designed to determine the proper solvent for removing residual NMP from the oligomer. Five solvents were chosen based on cost and mutual solubility with NMP. The solvents included water, ethanol, 2-propanol, acetone, and benzene. These solvents were tested initially to verify the insolubility of Thermid 600 and subsequently to determine ease of removing the solvent from the oligomer.
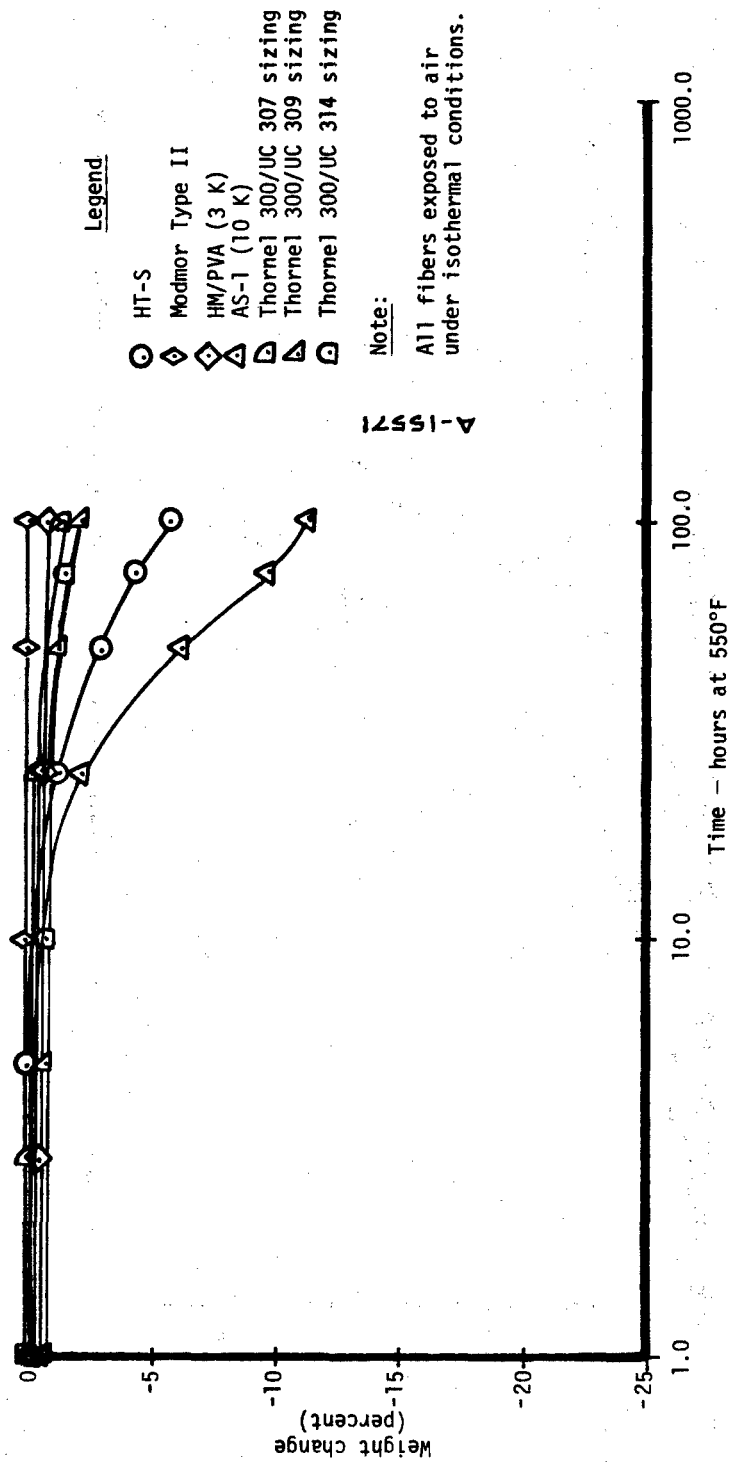
Figure 3. 550°F exposure fiber weight loss through 100 hours.

Legend

HT-S
Modmor Type II
HM/PVA (3 K)
AS-1 (10 K)
Thornel 300/UC 307 sizing
Thornel 300/UC 309 sizing
Thornel 300/UC 314 sizing

Note:

All fibers exposed to air under isothermal conditions.

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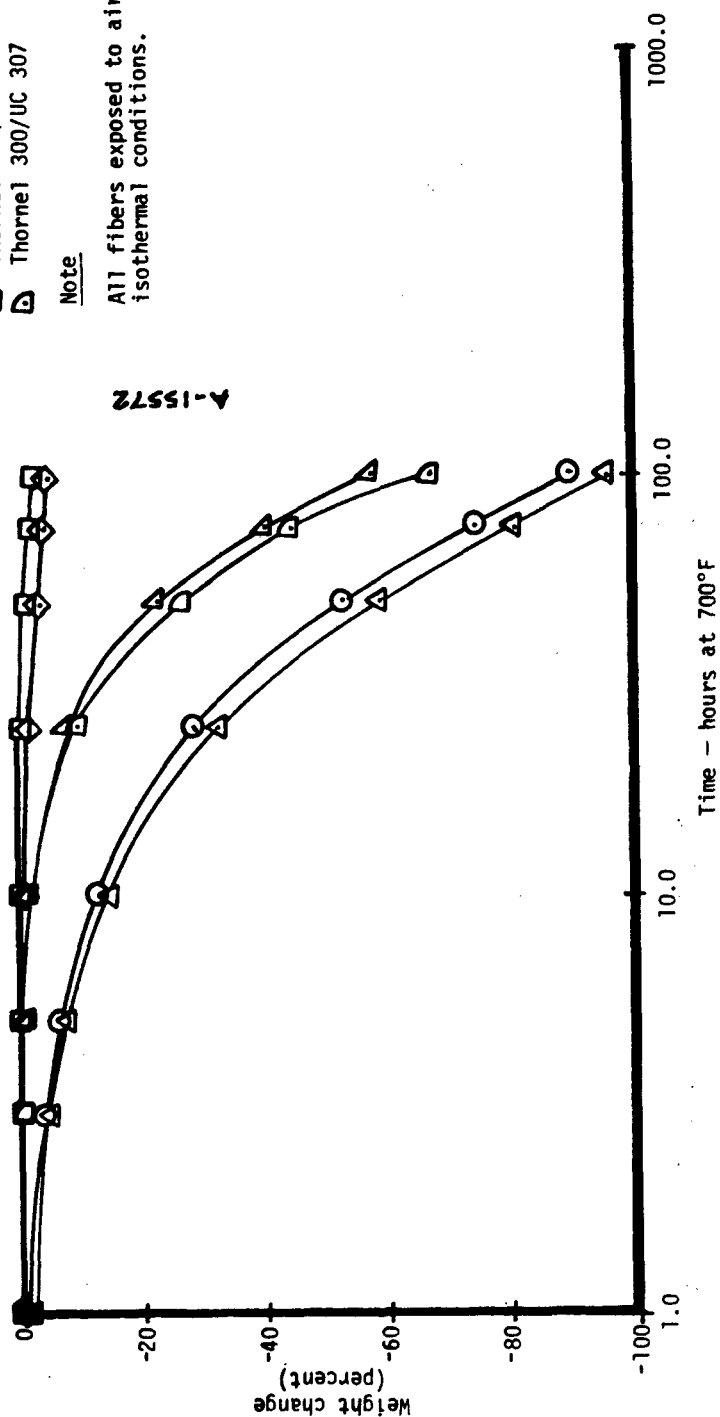
Figure 4. 700°F exposure fiber weight loss through 100 hours.

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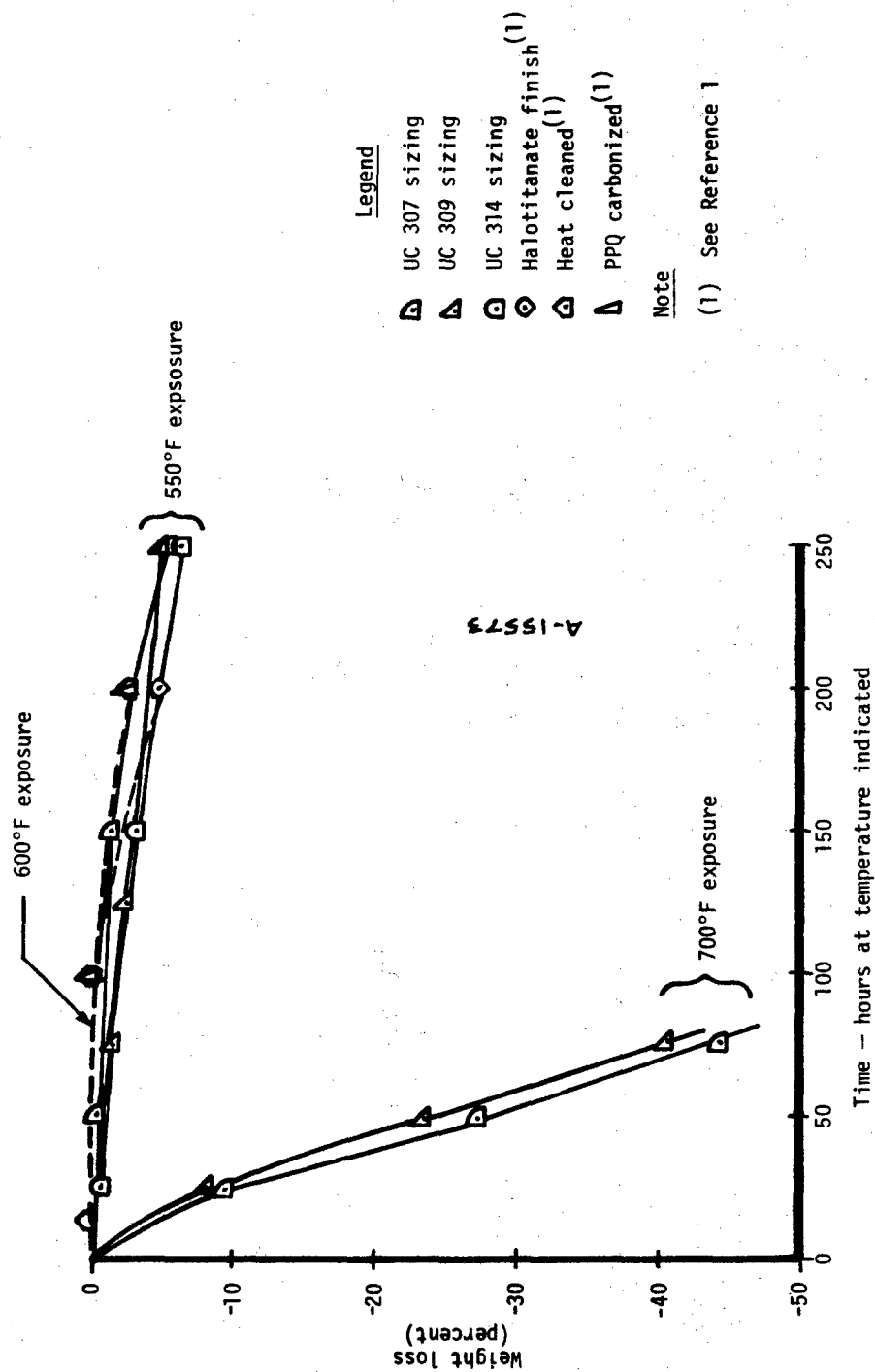
Figure 5.   Thornel 300 thermal oxidative stability -- effect of temperature and surface modification.

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TABLE 2. GRAPHITE FIBER PROPERTY DATA SUMMARY

Fiber Identity	Surface Condition	Lot Number	Filaments per Yarn	Young's Modulus 10^6 (psi)	Tensile Strength 10^3 (psi)	Density (gm/cm^3)
Thornel 300[a]	UC 314	220-4	6,000	32.2	373	1.73
Modmor Type II	Surface Treated	C-258	10,000	38.0	355	--
HM-S	Surface Treated	55-3	10,000	50.9	392	--
GY-70[b]	Surface Treated	129	384	74.7	263	1.96
GY-70[b]	Surface Treated with Epoxy Sizing	144	384	76.7	241	1.96

[a]Grade WYP15-1/0

[b]Single end

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TABLE 3. THERMID 600 BATCH SUMMARY

Batch Identity	Resin Production History
LS 7173	Powder resin from DMF[a]/m-Cresol solvent process; procured and evaluated prior to program start
6G504	Powder resin from NMP solvent process; first batch procured under this program; processing difficulties encountered
6H512	Powder resin from NMP solvent process
Thermid 600-A[b]	Thermid 600 solution in NMP; container identified as 30 percent solids, removed from Gulf production run
Thermid 600-6[b]	55.6 percent ethanol cake; removed from Gulf production run
Thermid 6L606	Powder resin from NMP solvent process, found to have lower melting point than either 6G504 or 6H512
Thermid 7E1101	Powder resin from NMP solvent process; comparable to 6L606 in properties

[a]Dimethylformamide

[b]Part of Batch 6L606. This identity was established by Aerotherm for control purposes.

TABLE 4. THERMID 600 CHARACTERIZATION DATA SUMMARY

T-310

Aerotherm Control Number	Batch Number	Batch Size (grams)	Tg[a] (°C)	PMT[b] Fusion (°C)	PMT[b] Melting (°C)	Gelation Temperature (°C)	Gelation Time (sec)	NMP Solubility
LS-7173	LS 7173	227	-	-	200	250	>200	soluble within 1 hr.
6G504	6G504	4760	-	185	>300	250	105	not soluble after 1 hr.
6H512	6H512	100	-	204	260	230	200	<20 percent at 70°C
2-67C	Thermid 600-A[c]	275	-	193	209	227	270	-
2-70E	Thermid 600-6[d]	1738	-	191	207	233	160	~20% overnight with stirring
6L606	6L606	1500	-	195	204	230	175	15% to 20% overnight with stirring
HA5-94	6L606[e]	1165	-	198	202	209	256	~20% with mild warming
7E1101	7E1101	4762	-	193	200	230	115	-

Aerotherm Control Number	Batch Number	Volatiles Temperature (°C)	Volatiles Weight Loss (Percent)	DSC Analysis[f] Exotherm Onset (°C)	DSC Analysis[f] Exotherm Peak (°C)	DSC Analysis[f] Sample Size (milligrams)	NMR[g] Proton Ratio[2]	ITGA[h] Percent Wt. Loss
LS7173	LS7173	-	-	207	252	8.6	22:1	-
6G504	6G504	-	-	205	240	8.8	16:1	-
6H512	6H512	300	3.0	205	240	10.8	-	-
2-67C	Thermid 600-A[c]	300	3.8	208	238	7.2	-	-
2-70E	Thermid 600-6[d]	300	1.7	195	238	12.0	-	-
6L606	6L606	300	2.3	203	235	12.7	-	-
HA5-94	6L606[e]	300	1.8	205	240	11.4	-	-
7E1101	7E1101	300	2.0	202	248	10.8	-	-

[a] Glass transition temperature after 16 hours at 600°F.
[b] Polymer melt temperature.
[c] Characterization conducted on resin recovered from NMP solution. Total batch size was 1360 grams.
[d] Characterization conducted on total resin recovered from ethanol cake.
[e] Characterization conducted on sample from 1165g. Portion of 6L606 ethanol wash followed by 125°C dry in vacuum oven.
[f] Differential scanning calorimeter, run at 5°C/minute rise rate in nitrogen.
[g] Nuclear magnetic resonance; to be run if other data indicates a need.
[h] Aromatic: Acetylenic
[i] Isothermal gravimetric analysis

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The procedure for testing the suitability of each solvent was the same: 1 gram of Thermid 600 in NMP (batch Thermid 600-A) was washed with 8 grams of solvent at room temperature, filtered and dried overnight in a vacuum oven at 80°C. The mother liquor was investigated for coloration and dissolved solids. The dried filtrate was weighed and its gel time recorded.

The experiments indicated that the highest recovery of oligomer was obtained with water. Both acetone and benzene in combination with the NMP dissolved too much Thermid 600 to be efficient and were dismissed from further consideration. Ethanol and 2-propanol were almost as effective as water.

Subsequently, 200-gram portions of 30-percent Thermid 600 in NMP were thoroughly blended with 500 ml of water in a Waring blender and the solid removed by filtration. The solid was washed with an additional 500 ml of water and then dried in a vacuum oven. Thermogravimetric analysis of each batch was used to determine the drying conditions which would produce a volatile free oligomer with minimum residual volatiles. Drying overnight at 105°C did not affect the gel time of the resin, but yielded resin which still contained 3.8-percent volatiles. The majority of the volatiles are lost between 130°C and 200°C, indicating removal of bonded water in addition to residual NMP.

An infrared spectrum of this oligomer showed a small amount of N-H absorption at 3300 cm^{-1}, and possibly a fourth carbonyl band at 1700 cm^{-1}. However, these are minor absorption bands and might represent hydrolysis of not more than 10 percent of the imide structure. Complete hydrolysis of the Thermid 600 oligomer to the corresponding amic acid would increase the weight of the oligomer by 6 percent.

Ethanol was chosen for the subsequent workup procedures (Reference 2). The ethanol cake (batch Thermid 600-6), when dried under Gulf's conditions, gave a powder containing 2.3-percent volatiles. This same cake was washed once more with ethanol and vacuum-dried overnight at 105°C. This provided a product with 1.7-percent volatiles and no NMP. Data from this characterization are presented in Table 4.

Subsequently, all of the remaining Batch 6L606 was washed with ethanol in the same manner and dried overnight at 125°C. The yield was 1165 grams of resin containing 1.8-percent volatiles. Results from the characterization of this material (HA 5-94) are compared in Table 1 for batches 6L606 and Thermid 600-A. The comparison indicates a very slight advancement of the resin with no decrease in volatiles for the additional 20°C employed in the drying operation. As in Batch 2-70E, most of the weight loss occurred between 150°C to 175°C.

Figure 6 shows the DSC analysis of the as-received Batch 6L606, and Figure 7 shows the DSC analysis of the Aerotherm-processed ethanol cake portion of 6L606. The size of the endotherm peak which occurs prior to the reactive exotherm is the only major difference between the two spectra.

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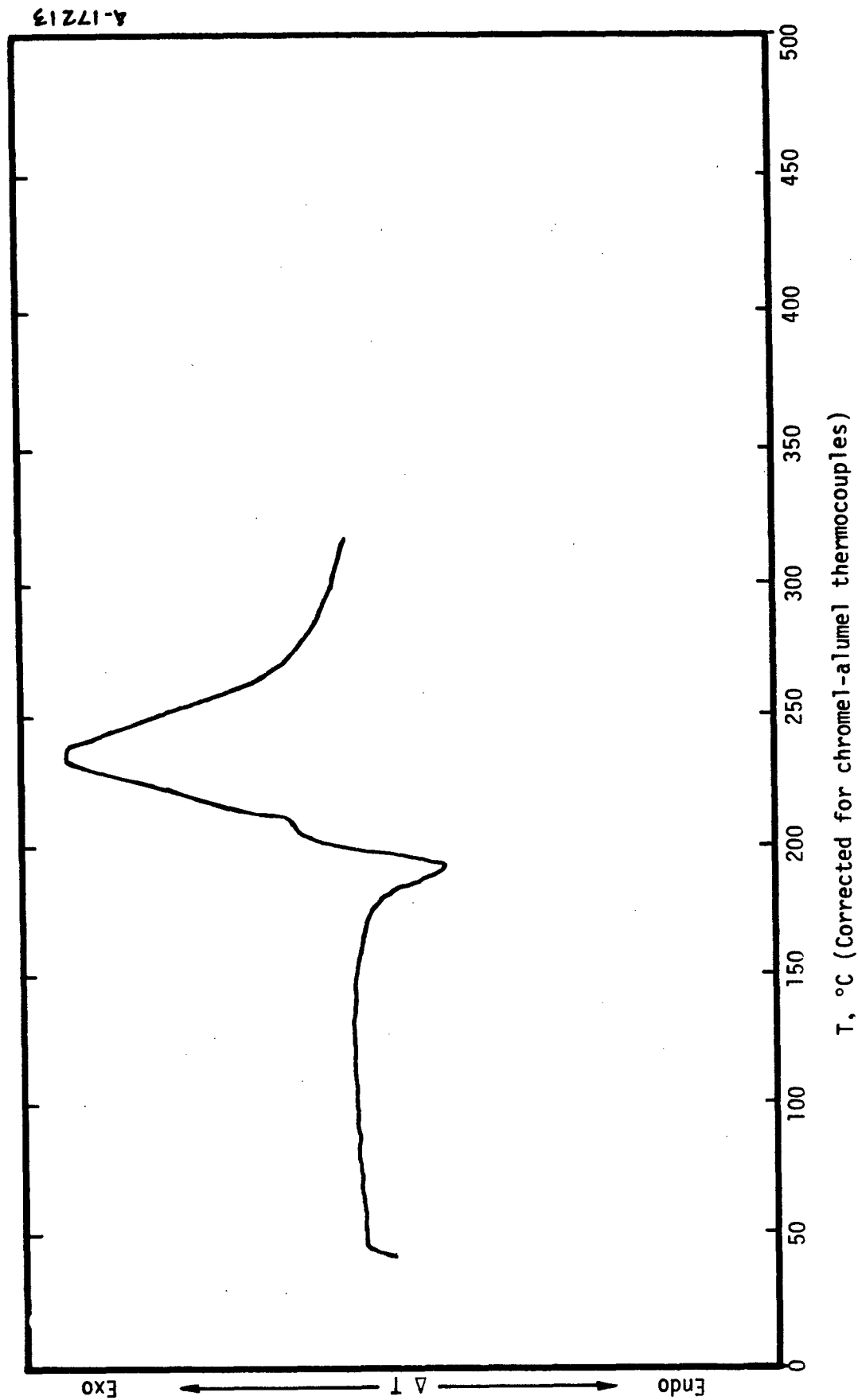
Figure 6. Thermid 600 batch 6L606 DSC curve.

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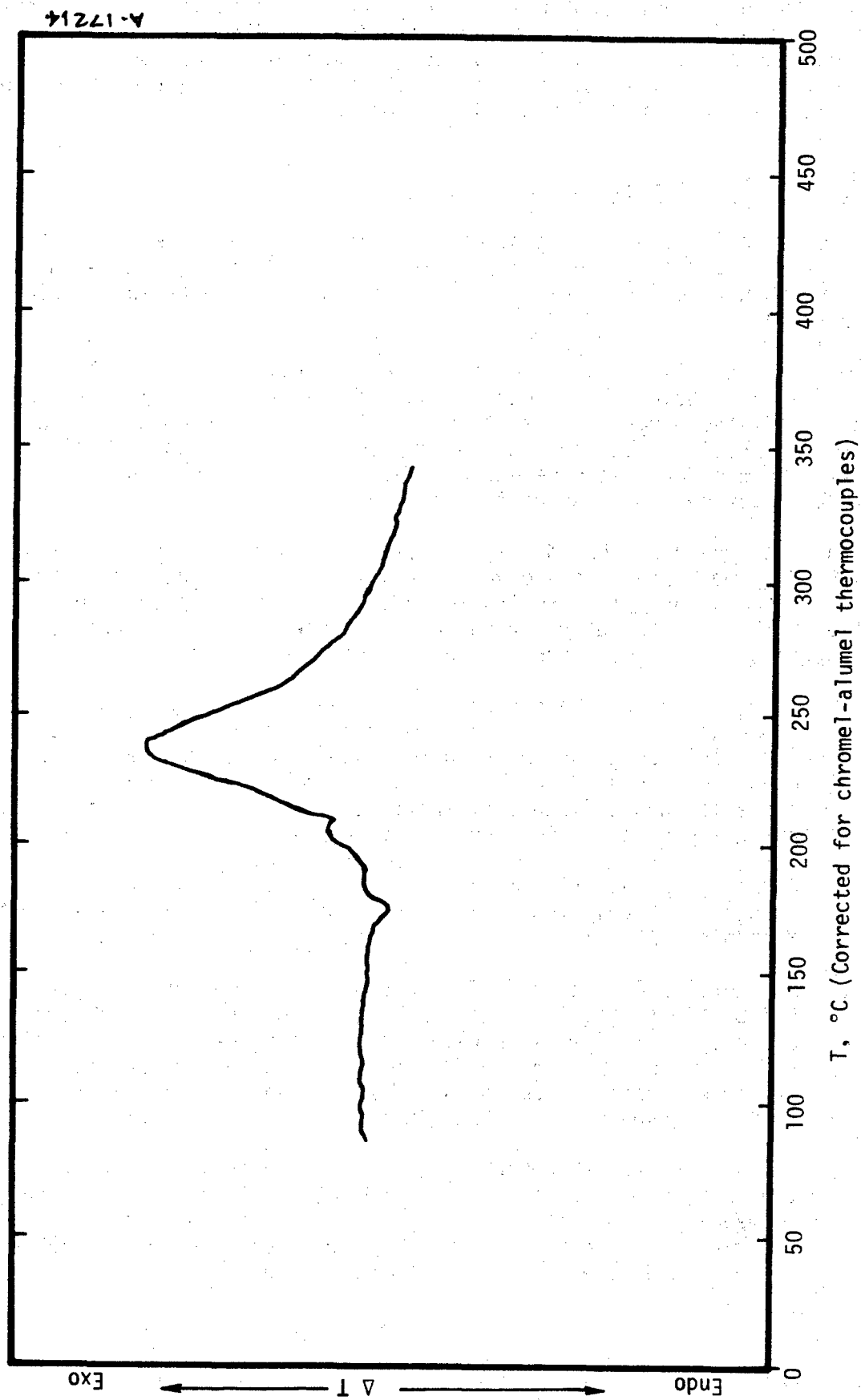
Figure 7.   Thermid 600 batch 2-70a DSC curve.

T, °C (Corrected for chromel-alumel thermocouples)

Exo ← ΔT → Endo

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All three products from Gulf Batch 6L606 (the reaction mixture, the wet cake and the dried product) had the same initial flow properties at 204°C (determined on the Fisher Johns) regardless of workup method, drying conditions, on residual volatiles. This is potentially significant, since it permits flexibility in the oligomer isolation methods.

Polyimide Moisture Stability Assessment

The general response of polyimides to moisture was assessed at the same time that Thermid 600 deliveries were characterized. The assessment focused on laminate data in available literature. Resin data was considered where pertinent.

Moisture stability data are sensitive to a number of variables. Typical variables include test specimen quality, exposure conditions, and detailed test methodology. Due to this sensitivity, no attempt has been made to assess data validity between the various sources. Instead, the reported trends within each data set were emphasized. Trends within each data set were evaluated by percent changes from control values.

The data reviewed showed a wide divergence in polyimide performance when exposed to moisture. This divergence was expected, since data for a number of different polyimide resins and reinforcements were considered. As presented in the representative trends discussed below, the divergence ranged from reported strength increases to significant degradation.

- Cray and Taylor (Reference 3) reported a 15-percent room temperature flexure strength increase with an RAE polyimide/A-1100-finished glass fabric after 14 days exposure. Exposure conditions were 90-percent relative humidity at 100°F. This same system showed a flexure strength loss of 14 percent after 7 days and a 7-percent gain after 21 days exposure.

- Farrisey, et al. (Reference 4) reported no dimensional or weight change for a polyimide 2080 molding after 7 days in boiling water. Mechanical property data for the molding were not given.

- Monsanto in Reference 5 (for Skybond 700 laminates with Style 181 A-1100-finished glass cloth) reported 2-percent water absorption after 24 hours immersion with vacuum-bag processing. They also reported a 0.7-percent absorption for high-temperature/high-pressure processed laminates. However, no mechanical property data are given for these conditions.

- Shepard, et al. (Reference 6), reported on their work with PDA-type polyimides reinforced with Hercules AS fibers. Their data showed a 4.2-percent reduction in flexure strength and less than 1-percent loss in short beam shear strength in comparing 550°F properties before and after a 2-hour water boil.

- Hertz (Reference 7) reported laminate data based on the Skybond 703 and 710 polyimides with HT-S fiber exposed for 6 weeks at 120°F and 95-to 100-percent relative humidity. At 600°F, the HT-S/Skybond 710 flexure strength retained 79.8 percent of the control value, while the short beam shear strength retained 85.5 percent of the unexposed value. This is contrasted with the HT-S/Skybond 703 system which showed a 67.9-percent flexure strength retention but an 8.1-percent increase in short beam shear strength after the same exposure conditions.

- Bilow (Reference 8) reported 88-percent strength retention after 929 hours in a 90-percent relative humidity, 160°F environment for a modified Thermid 600 adhesive

2.2.3 Prepreg and Composite Development

The first year of this program evaluated:

- Solution-prepregged Thermid 600

- Hot-melt prepregged Thermid 600

- Layup procedures

- Prepreg quality by composite property testing

- Cure and postcure cycle effects

Each of these first-year efforts are discussed below.

Solution Impregnation

Batch Thermid 600-A was used in the initial prepreg development. This resin batch was received as an NMP solution, and Thornel 300 yarn was selected as the reinforcement.

The first prepreg preparation emphasized evaluating prepreg techniques. For the first prepreg batch (6-16), Thornel 300 was drum-wound onto a Mylar backing. After thoroughly stirring Batch Thermid 600-A, the resin content was determined to be 23.1-percent solids. This solution was then coated onto the drum-wound Thornel 300. The prepreg was air-dried 8 hours, and then dried in a forced air oven for 45 minutes at 350°F.

After drying, Prepreg Batch 6-16 was removed from the oven and examined. There was little resin penetration through the Thornel 300. Prepreg gel time was determined to be 3 minutes at 485°F.

The second prepreg batch (6-17) also used Thornel 300 and Batch Thermid 600-A. Prepreg methods were unchanged except for resin application. One-half of the Thermid 600 solution was coated on the wound Thornel 300. After moderate heating, the coated Thornel 300 fibers were removed from the

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Mylar backing and placed on porous Teflon-coated glass fabric (TX-1040). The remaining resin was then coated onto the exposed Thornel 300 yarns prior to drying.

Two drying conditions were evaluated for Prepreg Batch 6-17. First, a sample was exposed for 30 minutes at 200°F. The volatile content was determined by exposing the dried sample to 500°F for 1 hour. Volatile content was 12.95 percent. Second, a sample was dried at 350°F for 45 minutes, and then exposed to 500°F for 1 hour. Volatile content was 1.3 percent.

Prepreg drying was then completed at 350°F for 45 minutes. The Gulf NMP reaction mixture used to produce the prepreg resulted in a product with very poor handleability. The potential for successfully fabricated complex components by cost-effective means was judged very poor.

Prepreg Batch 6-17 was used in preparing the unidirectional laminate 6-17B described later in this section.

Hot-Melt Impregnation (Unidirectinal Tape)

Thermid 600 Batch 6L606 was used for the initial hot-melt prepreg work. This batch was in a dried powder form. Characterization data for Batch 6L606 is documented in Table 4. Thermid 600 Batch 6L606 was selected based upon the characterization data and initial processing studies which indicated the resin would flow under practicable time and temperature conditions. These data were discussed in Section 2.2.2. The initial reinforcement used in hot-melt impregnation was Thornel 300 with UC 309 finish. This prepreg was assigned batch number 6-26.

The Thornel 300 yarns were first drum-wound onto an Armalon backing. The drum-wound yarns were taped in place and removed from the winder for prepregging. Yarn coating was achieved by passing the Armalon-backed Thornel 300 through a hot-melt coater with a 0.009-inch setting. Blade temperature was approximately 480°F, and the Thermid 600 powder was used without adding solvent. No attempt was made to increase resin penetration by posttreatment since there were gaps and some loss of collimation in the prepregs. However, some resin penetration from the coated side through the yarns to the backing side of the prepreg was observed. The prepreg was also difficult to handle. Due to poor collimation no further work was done with this prepreg.

It was difficult to obtain good collimation and improved handleability from this process due to the minimal flow characteristics of the Thermid at 480°F. This approach would require developing a low-viscosity Thermid 600 product specifically tailored for hot-melt prepregging.

Hot-Melt Impregnation (Fabric)

The second reinforcement investigated for hot-melt impregnation was epoxy-sized Celion 3000. The Celion 3000 was impregnated in a 24-inch x 23-inch, eight-harness satin-woven fabric form. Films were prepared from

Thermid 600 Batch 6L606 for the initial fabric impregnation tests. These films were deposited on nonporous Teflon-coated glass fabric (Armalon). Film thickness was 0.020 inch. Celion 3000 fabric was then placed between the two Thermid 600 films. For this initial effort, the fabric was impregnated by approximating a heated roll pressure application method such as would be used in a production environment. This approximation consisted of placing the Armalon-coated prepreg between 450°F preheated press platens for 20 seconds at 100 psi. The resulting prepreg appeared to have good resin penetration and retention of fiber collimation. Prepreg batch identity was 11-10.

Prepreg quality was verified by fabricating small composites. This is discussed below. Subsequent attempts to produce quality prepregs using the hot-melt approach showed that fiber bundle penetration was incomplete. This led to two significant efforts. The first was a further investigation of the flow and gel characteristics needed to achieve quality Thermid 600 prepregs. The results of this investigation are described below, following the discussion of layup and cure/laminate efforts. The second effort was to identify a Celion 3000 reinforcement system which permitted easier hot-melt prepregging and which retained the handleability advantages of the woven fabric. This second effort is currently in progress.

Layup Procedure

In the layup procedure for all prepregs, Teflon-coated glass fabric was used (TX-1040) as a separator. Fiberglass Style 116 fabric was used as the bleeder. These selections were made to minimize variables which might be introduced by using developmental materials. The layup was placed in a trap mold and instrumented with a thermocouple prior to start of curing.

Cure/Laminate Procedure Development

Initially, testing was conducted to assess cure and prepreg quality by evaluating resin-sensitive parameters. The short-beam shear test was selected for this effort. This permitted cure cycle effects to be analyzed using small amounts of resin and prepreg. Composites fabricated and results obtained are discussed below.

Solution Prepreg Composites

A 2-inch x 2-inch, 11-ply unidirectional layup of Prepreg Batch 6-17 was prepared for cure by the procedure described above. The completed layup was placed in a trap mold and instrumented with a thermocouple. The following steps describe the cure cycle:

1. Place into press preheated to 485°F

2. Apply contact pressure for 1 minute

3. Release pressure each 10 seconds (bump) for 30 seconds

4. Increase pressure to 200 psi over 5 minutes

5. Hold at 485°F under 200 psi for 2 hours

6. Cool under pressure to below 200°F

When removed from the mold, Laminate 6-17B was trimmed, weighed, and examined visually. Resin content was 31.75 percent and specific gravity was 1.56. Thickness was 0.079 to 0.081 inch. The laminate appeared to be free from macroscale defects such as cracks and porosity.

Eight short-beam shear specimens were machined from Laminate 6-17B. Four of these specimens and the unmachined portion of the laminate were stored in a desiccator. The remaining four short beam shear specimens were then postcured for 24 hours at 600°F in a nitrogen environment. These specimens were also placed in the desiccator and stored until tested.

The short-beam shear test results are provided in Table 5.

These strengths are adequate but should not be considered optimum for the Thermid system. The postcure schedule of 24 hours in nitrogen did not affect the room-temperature shear values significantly.

It can be concluded that the solution prepregging method provides simple, quality laminates and that the cure schedule described above is useful for obtaining small laminates.

Hot-Melt Prepreg Composites

Hot-melt Prepreg Batch 11-10 was layed up (five plies) using the layup procedures previously described. The following cycle was then used to cure the laminate:

1. Place mold into cold press

2. Apply contact pressure and start press to 485°F

3. Apply 200 psi when layup is at 400°F (~15 minutes)

4. Hold at 485°F for 1.5 hours

5. Cool under pressure to below 200°F

This cycle is significant since the "bumping" required for solution prepreg has been omitted.

The resulting 2-inch x 2-inch, five-ply Celion 3000 fabric laminate had excellent visual quality and low flow. Eight short-beam shear specimens were then machined from Laminate 11-10A. Four of the shear specimens and the remaining panel section were placed in a desiccator for storage. The remaining four shear specimens were postcured for 16 hours at 600°F under nitrogen in a free-standing state. The eight specimens were then tested.

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TABLE 5. UNIDIRECTIONAL T300/THERMID 600 LAMINATE TEST RESULTS

Laminate[b] Identity	Postcure	Specimen Number	Test Temperature (°F)	Shear Strength (ksi)
6-17B	--	1	70	11.8
	--	5	70	13.6
				12.7 Avg
	--	6	500	4.8
	--	8	500	5.5
				5.2 Avg
	a	2	70	12.2
	a	4	70	10.2
				11.2 Avg
	a	3	500	5.9
	a	7	500	6.9
				6.4 Avg

[a] 24 hours at 600°F in nitrogen

[b] Solution prepreg used

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The Thermid short-beam shear test results with this fabric are presented in Table 6. After the 485°F cure for 1-1/2 hours, an average of 7600 psi was obtained. The maximum of 8200 psi agrees with that obtained with a high-performance epoxy resin system. It is concluded that Thermid 600 with Celion fabric is capable of providing approximately the same short-beam shear strengths as obtained with epoxy resin systems.

The reduction shown in Table 6 for the room temperature shear strengths of Laminate 11-10A after 16-hour postcure is not understood. However, we have observed the same phenomena with other systems which have been given an unrestrained postcure where the postcure schedule is executed too rapidly. The resin softens and undesirable effects are seen in the composite when the postcure is too rapid.

Processing Review

Thermid 600 processing was reviewed with Mr. Arturo Castillo and Dr. Boyce Kimmel, Hughes personnel. The following paragraphs summarize this review.

The processing method used by Hughes for Thermid 600 involved placing the layup into a preheated 485°F press. This point was discussed extensively, since inserting large layups into such a processing sequence would be extremely difficult to control. The primary control difficulty would be heatup rate differences due to heat sink effects of large components compared to small layups in a laboratory press.

A manufacturer would prefer to use his existing equipment for processing. Typically, a layup is placed into a cold autoclave or press and the maximum heat rise attained from the equipment used. Maximum heat rise for large-scale standard autoclaves do not typically reach 10°F per minute. Heat rises of this magnitude, however, can be achieved by placing the layup into the preheated autoclave if the tooling mass is not substantial.

Aerotherm fabricated low-void Thermid 600 composites from the 24-inch x 23-inch, eight-harness satin fabric using a 14°F per minute heat rise from room temperature to 485°F in a press autoclave. This technique should be acceptable to an aerospace hardware manufacturer. However, the heat rise used was probably in excess of standard commercial autoclave capabilities.

Mr. Audie Price, Aerotherm Manufacturing Director, consultant to this program, suggested known minor autoclave modifications as an acceptable approach to achieving up to the 15°F per minute heat rise. Such modifications would not be expensive.

The next major milestone for Thermid systems would be to demonstrate suitability for fabrication using heat rise rates of less than 14°F per minute. Conventional autoclave processability would be represented by a resin which could be used with equipment which is presently on hand by manufacturers and may not be capable of more than 3°F to 5°F per minute heat rise.

TABLE 6. CELION 3000 24 x 23 FABRIC/THERMID 600 LAMINATE
TEST RESULTS

Laminate[b] Identity	Postcure	Specimen Number	Test Temperature (^{O}F)	Shear Strength (ksi)
10-10A	--	1	70	6.9
	--	6	70	8.2
				___
				7.6 Avg
	--	3	500	4.2
	--	8	500	4.9
				___
				4.6 Avg
	a	2	70	3.2
	a	5	70	5.3
				___
				4.3 Avg
	a	4	500	5.6
	a	7	500	2.8
				___
				4.2 Avg

[a]16 hours at 600°F in nitrogen

[b]Hot-melt prepreg used

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Due to the limited solubility of Thermid in NMP, tack cannot be induced into the prepregs by using excess solvents such as seen with some polyimide prepregs. The Thermid-solvent prepregs are nearly identical to the hot-melt prepregs in that they are boardy with only moderate drape and no tack. Excess NMP is found as a liquid on the surface of the prepregs. Hughes' solvent prepregs typically contain 3-percent volatiles based on the weight of the prepreg.

Gel and Flow Properties for Hot-Melt Prepregging

As previously noted, several unsuccessful attempts were made to achieve fiber bundle penetration by hot-melt prepregging the 24-inch x 23-inch, eight-harness satin Celion 3000 fabric at 248°C (480°F). Guidelines were established for judging complete success of prepregging and for assuring cost-effective production. The guidelines are listed below:

- Ninety-percent retention of the gel life of the Thermid resin

- One thousand feet per day with a 2-foot minimum width

- Excellent fiber wetting

- At least 40-percent resin pickup

- No degradation of the graphite reinforcement

During this effort, it was discovered that when prepregging temperatures in excess of 280°C were investigated, a clear, nonopaque melt was observed upon cooling. At normal prepregging temperatures, 245°C, an opaque melt formed. This opaque melt was attributed to crystallinity in the Thermid and led to reexamining Thermid 600 prepreg parameters. Accordingly, gel time and flow properties were systematically determined at temperatures up to 300°C.

Figure 8 shows the gel times (Fisher Johns) of four Thermid 600 batches received from Gulf. These times are plotted against increasing temperature. Each point shows the average of five determinations. Values for Batch 6G504 and 6H512 were not taken at 225°C because complete melting was not observed for these oligomers at that temperature. Since these values were to be baseline for the Thermid 600, the temperatures were corrected against melting point standards.

The closeness of the curves indicates that gel time reproducibility is excellent for Thermid 600 on these four Gulf batches. Earlier gel-time determinations did not show this reproducibility. The previous lack of reproducibility was probably due either to measurement at too low a temperature for clear end point detection or the lack of test repetition to obtain an average. Table 7 presents the average gel time values at 275°C.
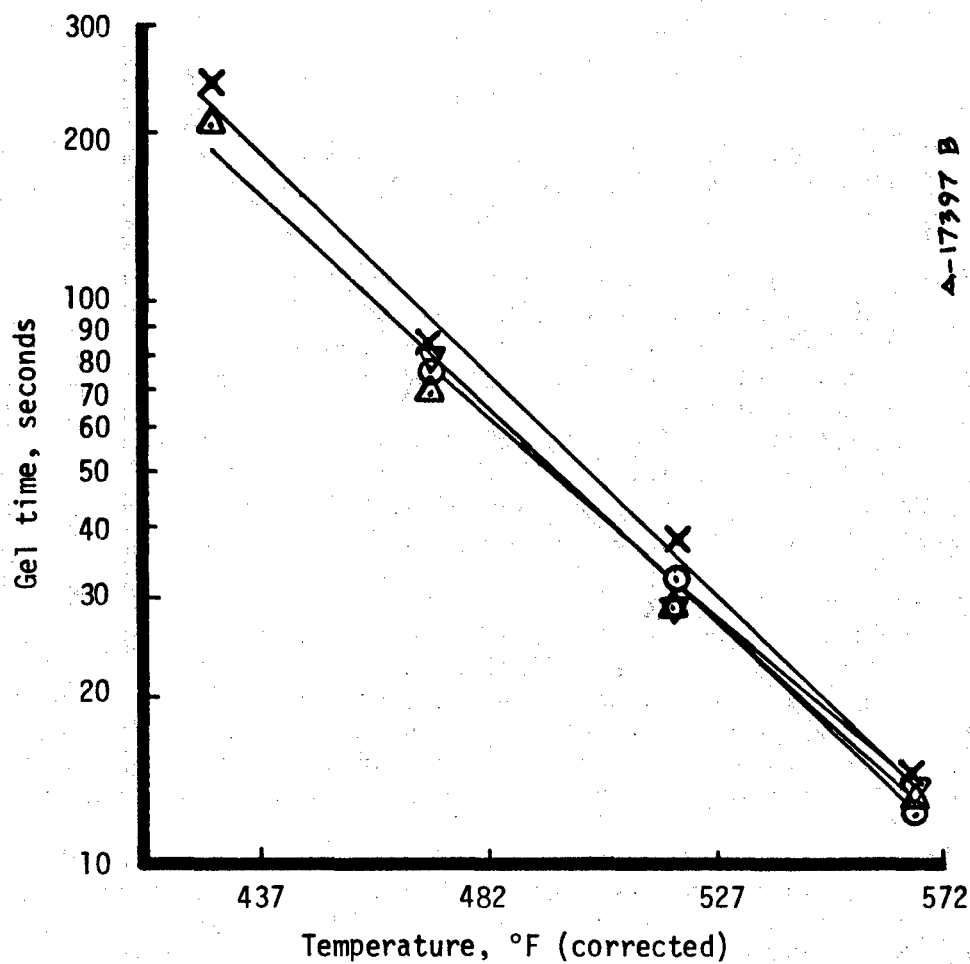
Figure 8. Gel times of Gulf Thermid 600.

TABLE 7. AVERAGE GEL TIME VALUES AT 275°C FOR THERMID 600

Batch No.	Gel Time, Sec
LS7173	36.9[a]
6G504	31.9
6H512	28.8
6L606	28.9[a]

[a]Measurable gel time at 225°C

The gel-time end points at both 275°C and 300°C are easily observed due to the rather sharp transition from the molten polymer to the rubbery state.

The flow characteristics of the resin samples were determined by placing 1.0 gram of powdered resin on aluminum foil on a press platen. Both press platens were at the test temperature. The sample was immediately covered with a second piece of aluminum foil, coated with Frecoat 33 release agent, and the press was closed. Fifty-psi accumulator pressure was rapidly applied to the sample and the flow time started. At the end of 2 minutes, the pressed-out polymer was removed from the press, cooled, and the diameter of the disk recorded. If the pressout was elliptical, the average of the minimum and maximum dimensions was recorded.

Flow characteristics as evaluated by measuring pressout diameters for Thermid Batch 6L606 are shown in Figure 9. The measured pressout diameter maximums and minimums obtained are indicated at each temperature for the five replicates. The upward slope clearly demonstrates the expected increase in pressout diameters (decrease in viscosity) with increasing temperatures. The nearly linear diameter/temperature relationship indicates that gel onset did not reduce the flow process at higher temperatures as one might expect.

Solvent content, aging conditions, and particle size of the Thermid prepolymers are additional factors likely to influence the pressout diameters obtained at a prescribed temperature. We intend to achieve reproducible flow properties of the batch-to-batch prepreg product. These variables, in addition to the flow properties of the as-received Thermid product, need to be addressed.

These studies led to further investigation of those processing conditions which would provide quality prepreg with minimum loss of Thermid 600 gel time, and retention of acceptable flow properties.

Polymer advancement by drying, prepregging or other thermal treatments resulted in shortened gel time. Resin advancement was monitored as a percentage of the original as-received gel time.
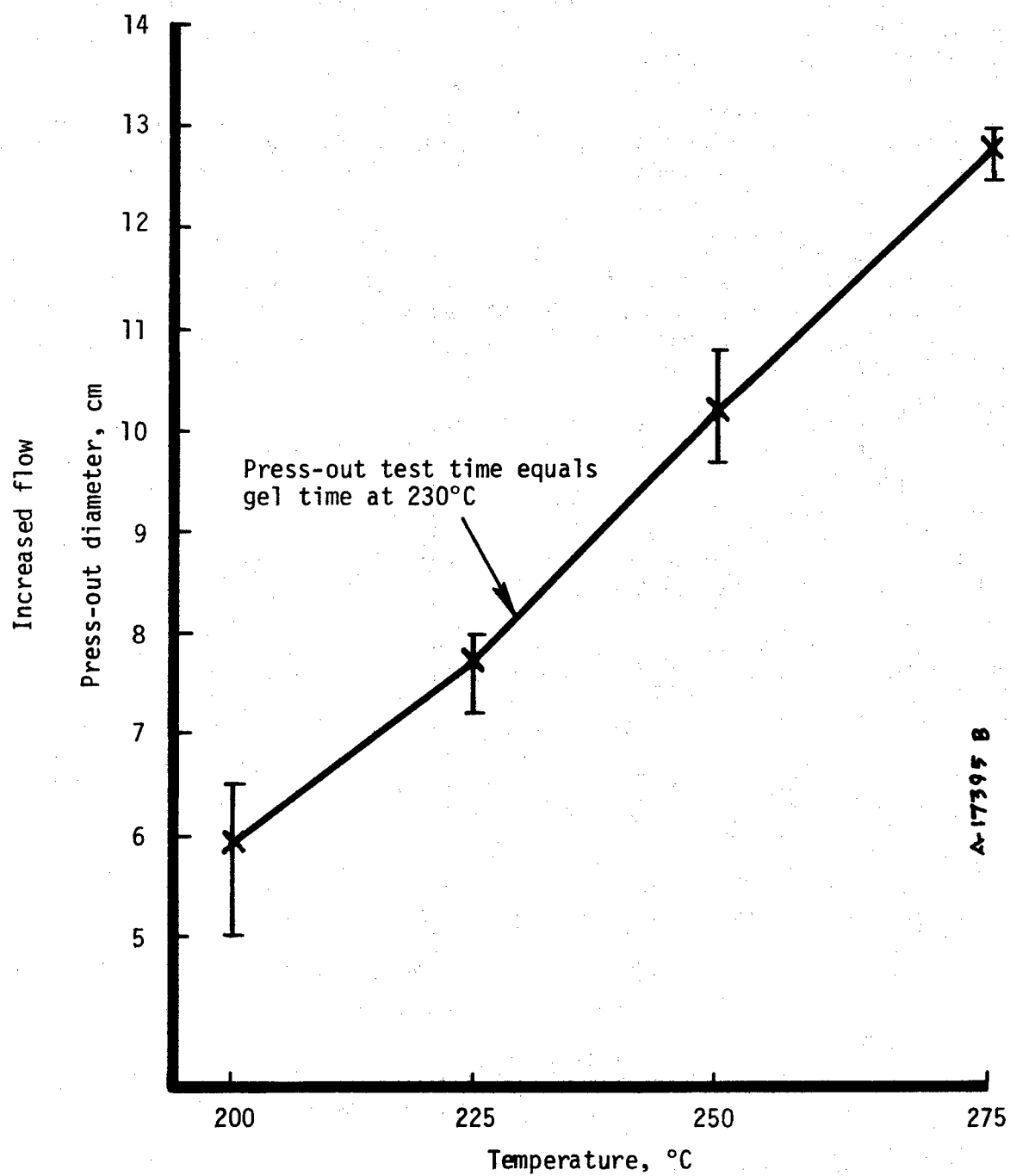
Figure 9.   Thermid 600 batch 6L606 flow evaluation.

Treating Thermid 600 for 1 to 2 seconds at 310°C (590°F) retained only 30 to 50 percent of the original gel time. Eighty-five to ninety-five percent retention had been expected. The difference was caused by exposing the resin to additional heat during cooldown of the Thermid 600. Forced cooling immediately after the 310°C (590°F) exposure provided gel time retentions of up to 90 percent.

In this evaluation, powdered Thermid 600 was placed between release films and pulled through a hot press as shown in Figure 10. Those conditions which resulted in 90-percent retention of gel time are identified in Table 8.

Maximum resin content achieved with these conditions was approximately 25 percent, much lower than expected. The volatile content of the Thermid 600 caused the low resin content; volatiles were less than 2 percent. However, at this temperature the volatiles caused serious resin foaming and resin loss from the prepreg.

DSC analyses of the starting material (HA-5-93) and the samples processed at 20, 12, 6.7, and 5.0 feet per minute are provided in Figures 11 through 15, respectively. Heat treatment clearly eliminated the endotherm observed at 185°C. The endotherms observed at 198°C and 215°C are more diffuse and eventually disappear (Figure 15), showing a 62-percent retention of the gel time. The exotherm onset for this Thermid sample is only 150°C and is nearly identical to the DSC of ATQ.

Flow characterization by pressouts of the 310°C (590°F) processed Thermid 600 has provided the very promising results described below.

Pressouts were conducted on 0.88-gram samples of the Thermid 600, prepared as described. Flow characterization by pressouts were conducted on the same samples used in generating the data presented in Table 8. Diameters obtained in the flow characterizations are shown in Table 9 and were obtained at 250°C (482°F).

2.2.4 Summary of Thermid 600 Development Efforts

The following tests have shown that Thermid 600, produced by Gulf Oil Chemical Company, appears to have good batch-to-batch reproducibility:

● Gel time determination

● Flow properties evaluation at 250°C (482°F)

● DSC analysis

Volatile contents of typically less than 2 percent (by TGA analysis to 300°C) interfere with high-temperature prepregging by causing the Thermid 600 to foam. Thermid 600's low-temperature, flow properties at 200°C (392°F), are quite variable on a batch-to-batch basis.
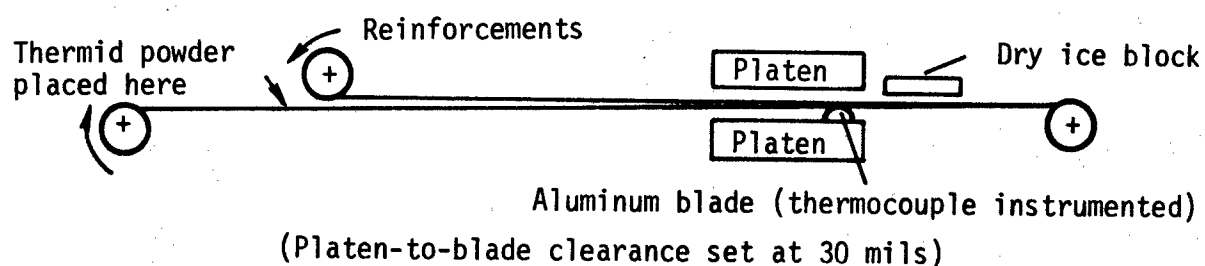
Figure 10. Thermid 600 prepreg production simulation.

TABLE 8. PREPREG PARAMETER EFFECTS ON THERMID 600 GEL TIME

Line Speed, ft/min	Time in Hot Zone, seconds	Gel-Time Retention, %
20	3	90
12	5	83
6.7	9	66
5.0	12	62
3.2	19	>5
2.4	25	Gelled in press
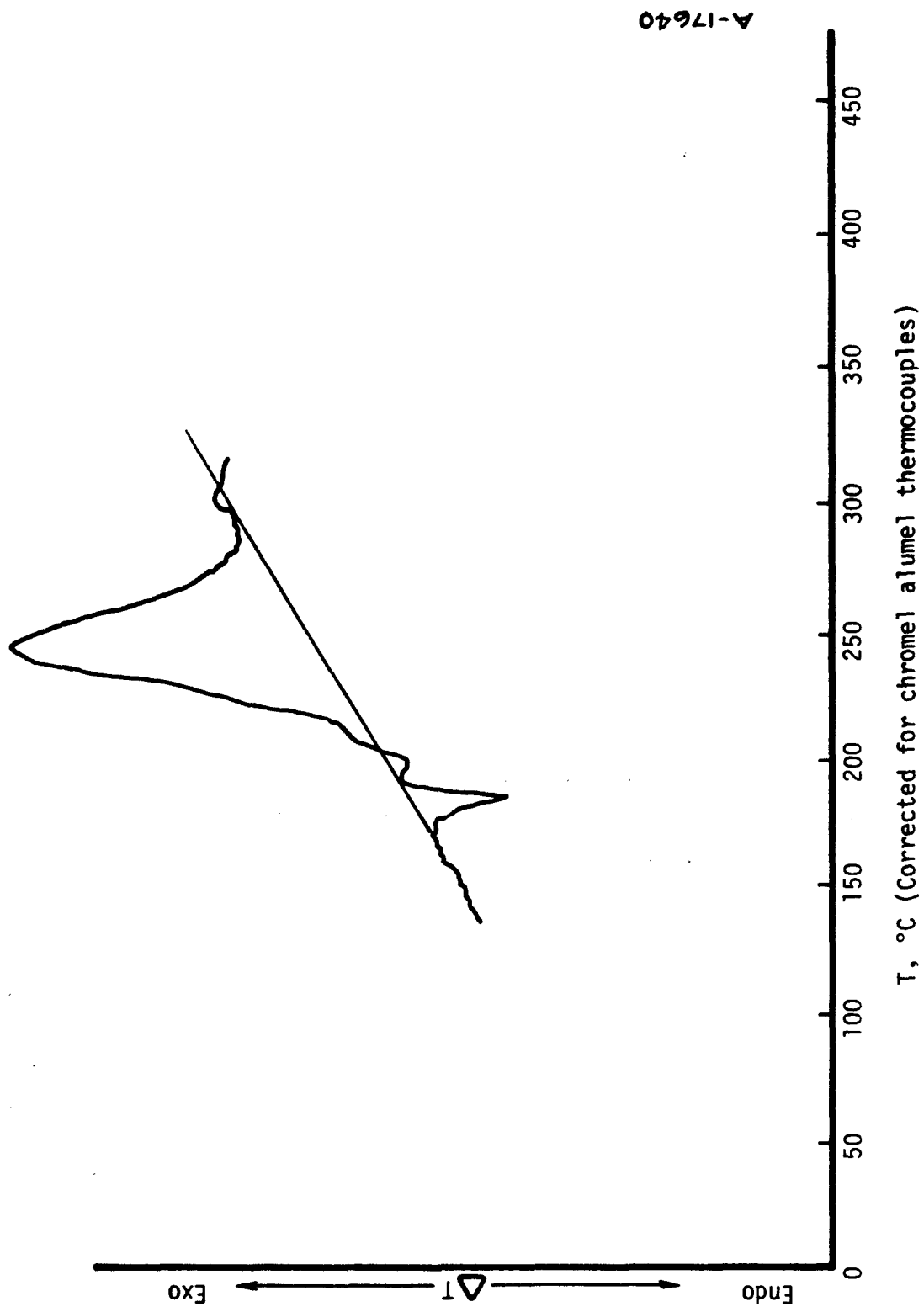
Figure 11. DSC analysis of Aerotherm processed Thermid 600 (batch 6).

A-17641
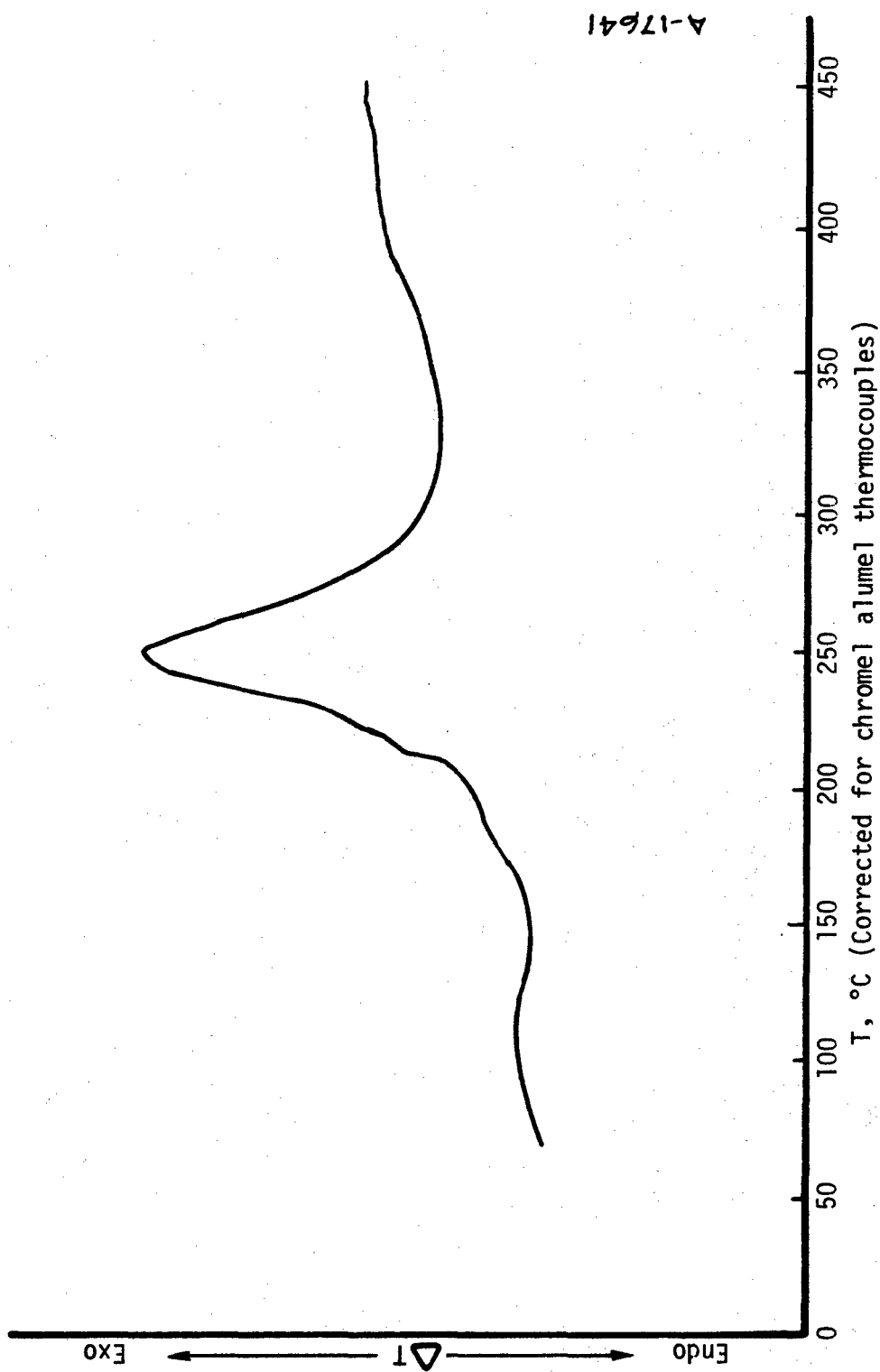
Figure 12. DSC analysis of Thermid 600 processed at 20 feet per minute.

T, °C (Corrected for chromel alumel thermocouples)

Exo ←——— ΔT ———→ Endo
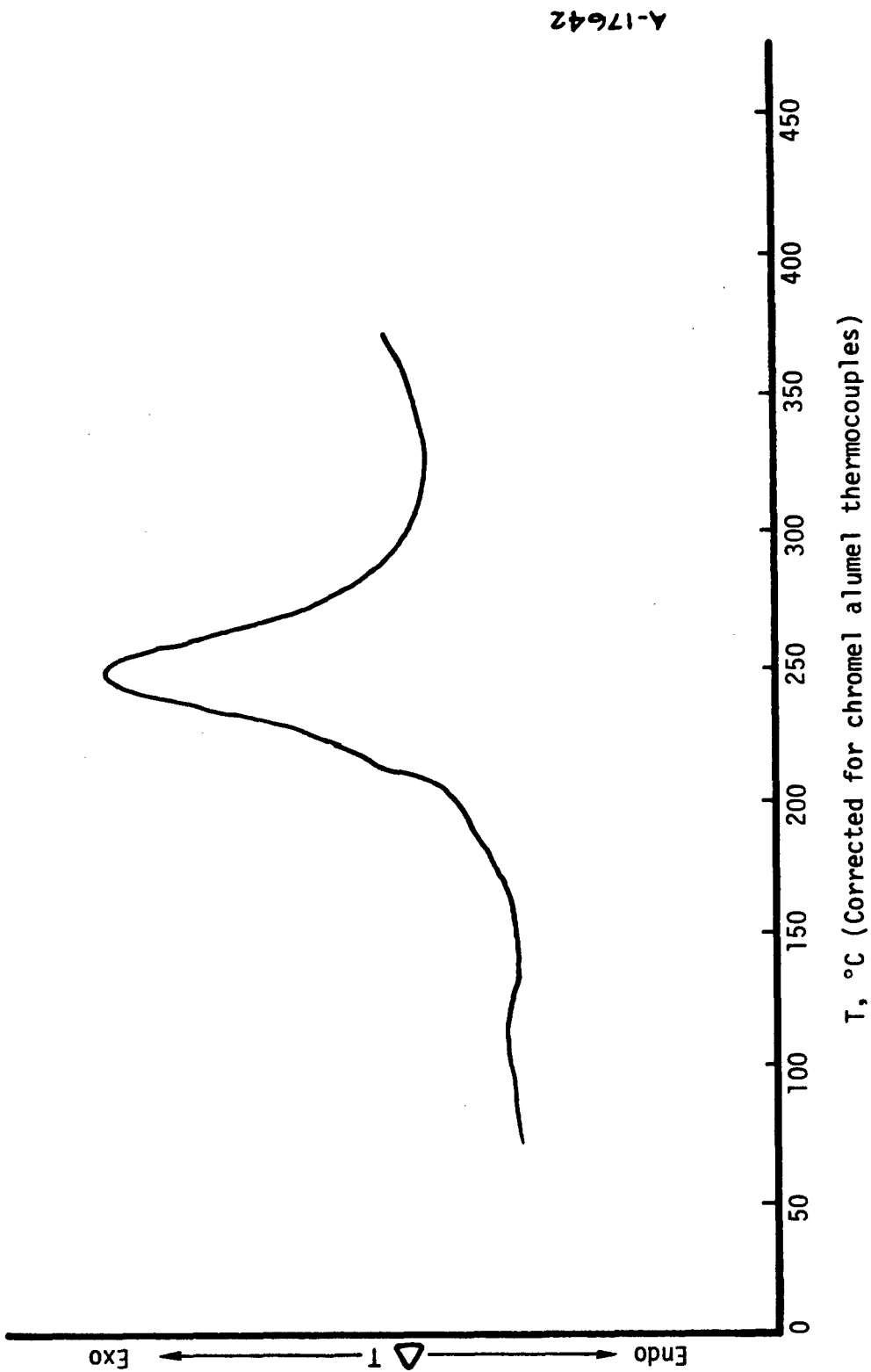
Figure 13. DSC analysis of Thermid 600 processed at 12 feet per minute.

34
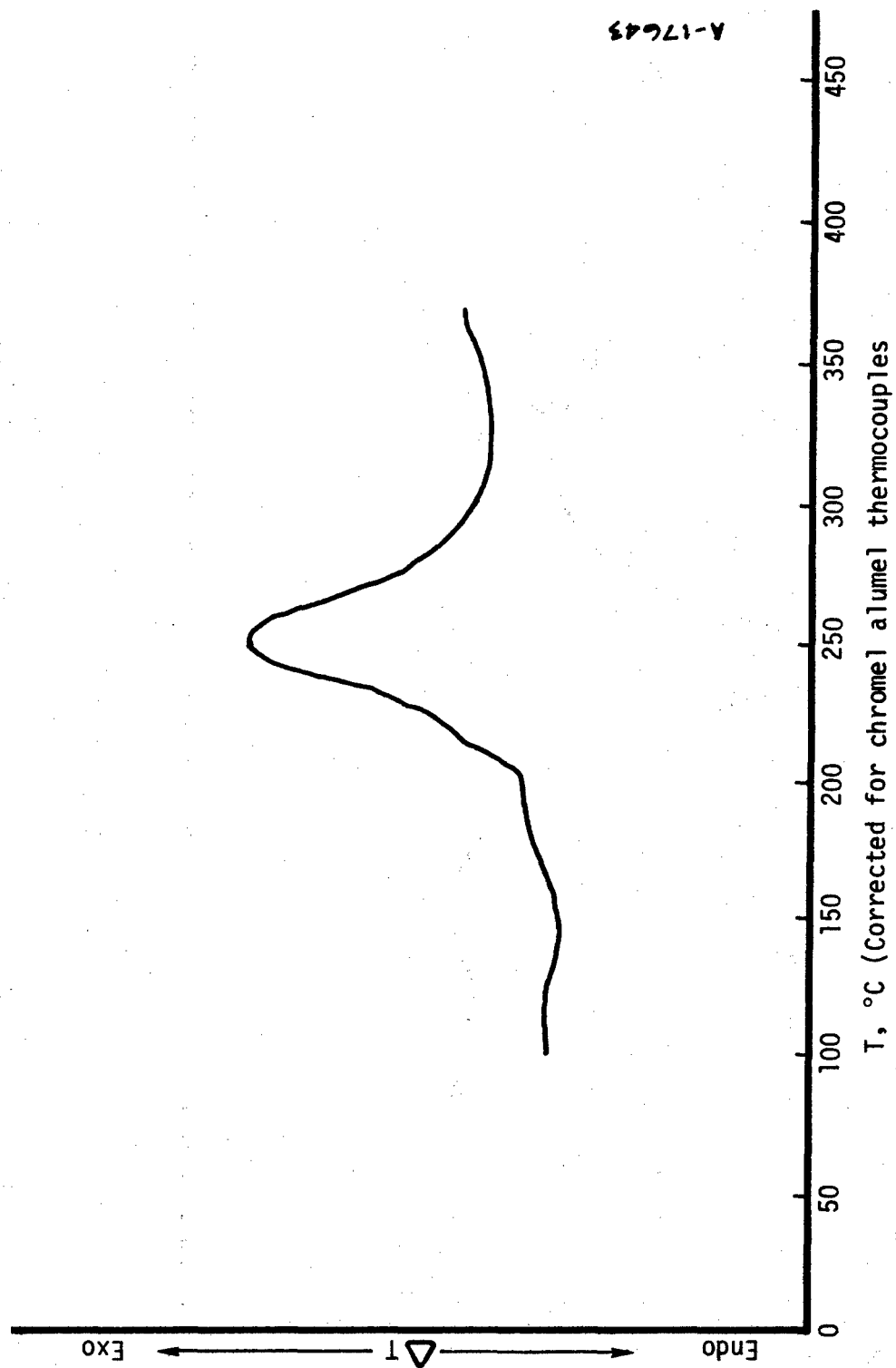
Figure 14. DSC analysis of Thermid 600 processed at 6.7 feet per minute.

A-17643
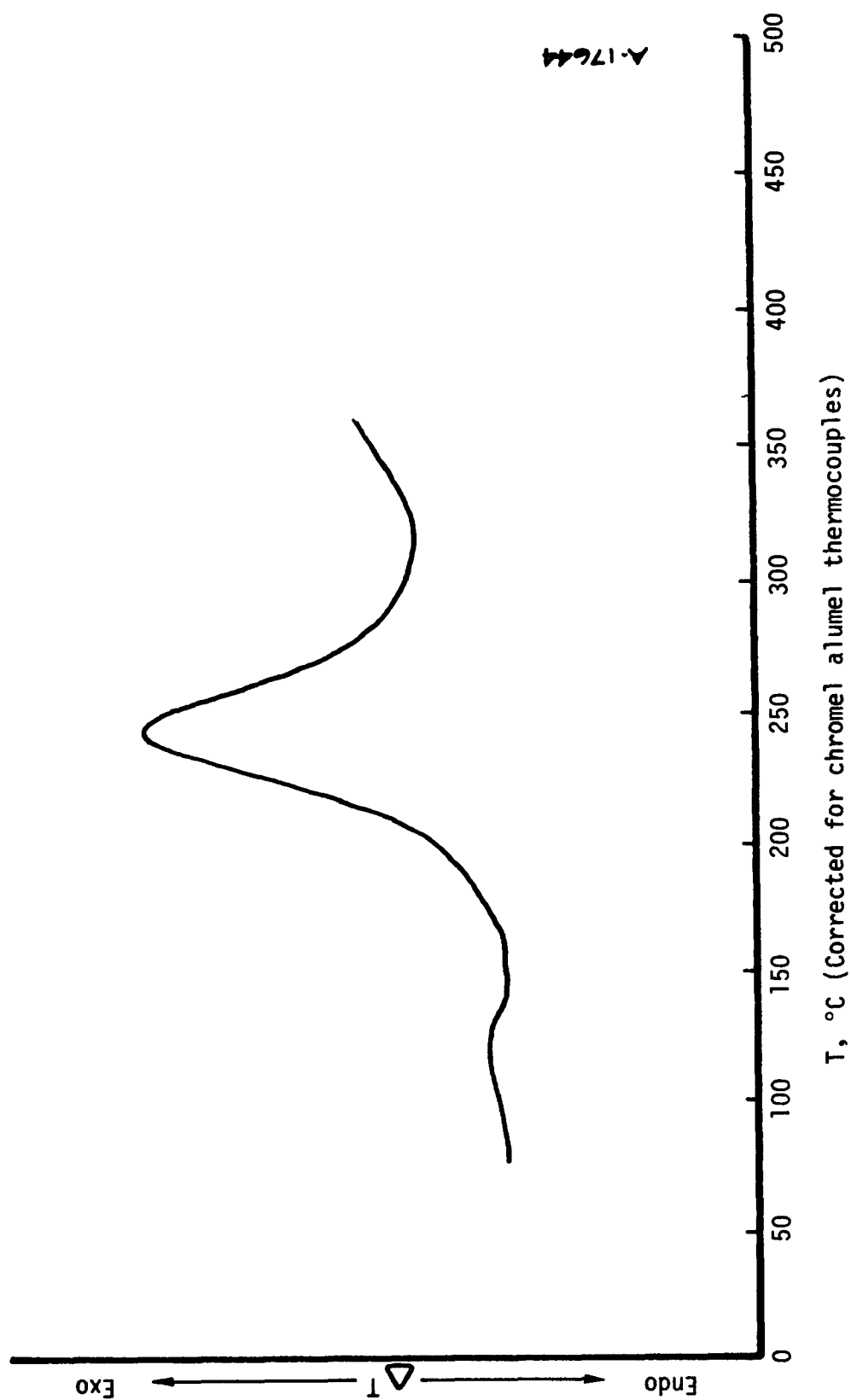
Figure 15. DSC analysis of Thermid 600 processed at 5.0 feet per minute.

TABLE 9. THERMID FLOW CHARACTERIZATION[a]

Sample	Pressout Areas, in^2
Thermid Starting Material	23.2
20 ft/min	21.2
5 ft/min	14.3
3.2 ft/min	4.7

[a]Conducted at 482^oF (250^oC) with same sample as used in Table 8.

In initial testing, Celion 3000 appears to be the fiber of choice for Thermid 600.

The possible benefits of various surface treatments for Celion were not investigated for use with Thermid 600. High-quality laminates were produced by both solution and hot-melt fabrication of Thermid 600 graphite prepregs. The advantages and disadvantages of both methods are listed below:

● Solution prepregging

Advantages	Disadvantages
-- Facile fiber bundle impregnation	-- Hot impregnation required
	-- NMP difficult to remove
	-- Danger of negating addition-cured merits of resin system
	-- Resin crystallizes with time giving a "powdery" prepreg

● Hot-melt prepregging

Advantages	Disadvantages
-- More economical than solution methods	-- Commercial hot-melt equipment
-- Low volatile prepregs virtually guaranteed	-- As-received Thermid 600 still contains volatiles
-- Clear noncrystalline resins produced	

The hot-melt process is the method of choice for preparing Thermid 600 graphite prepregs.

Heat treating the as-received Thermid 600 produces a clear resin system which has better flow properties at 204°C (400°F), but equivalent flow properties to the non-heat-treated polymer at 250°C (482°F). This is attributed to removing the crystallinity from the as-required Thermid 600. DSC analysis of the two polymers confirms this.

Autoclave processing was demonstrated for production of Thermid 600 graphite composite at a heating rate of 14°F/minute. Slower heating rates are not indicated for use at this time. High-quality composites are virtually assured if the stacked, low-volatile prepreg is placed either in a hot (485°F) matched die mold or in a matched die mold at room temperature and heated very rapidly.

Low-volatile Thermid 600 prepregs appear difficult to prepare by hot-melt prepregging methods. However, the addition-cure feature of the resin

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system makes the processing advantages over conventional high volatile polyimides a most worthwhile objective. Thus, a prepreg product can be developed which would have no, or very low, volatiles.

2.3 ATQ DEVELOPMENT

Addition-cured acetylene-terminated quinoxalines (ATQ) were developed at the Air Force Materials Laboratory. Efforts conducted on this polymer system in the first year of this program included synthesis of the selected ATQ oligomer, its prepreg development -- including both solution and hot-melt approaches, and composite data that replicated previously reported AFML data.

When this work indicated a high cost for the initially selected ATQ's, attention was shifted to lower-cost ATQ structures. Initial efforts to develop the lower-cost ATQ oligomers are discussed in Section 2.4.

2.3.1 Reinforcement Selection

Reinforcement selection for ATQ graphite prepregs and composites was based primarily on anticipated use at 400°F to 550°F. Assessment of the thermal oxidative performance for a wide range of graphite fibers was presented in Section 2.2. This assessment indicates that Thornel 300, or other fibers meeting or exceeding the properties of Thornel 300, are acceptable for use with ATQ.

2.3.2 ATQ Synthesis and Characterization (First Structure)

The individual steps used for ATQ (first structure) synthesis are summarized in Figure 16. Appendix A provides experimental procedures for the following preparations:

- 4,4'-oxybisbenzil (OBB)

- 3,4-dinitrofluorobenzene

- β-chlorocinnamaldehyde-3-yl p-toluenesulfonate

- 3-ethynylphenyl p-toluenesulfonate

- 3-(3,4-dinitrophenoxy)phenylacetylene

- 3-(3,4-diaminophenoxy)phenylacetylene

- Benzil end-capped quinoxaline oligomer

- Acetylene-terminated quinoxaline (ATQ) oligomer

Purification of 3,3'-diaminobenzidine (DAB) is required for synthesis of both ATQ and PIQ. The experimental procedures used for DAB purification are given in Appendix C.
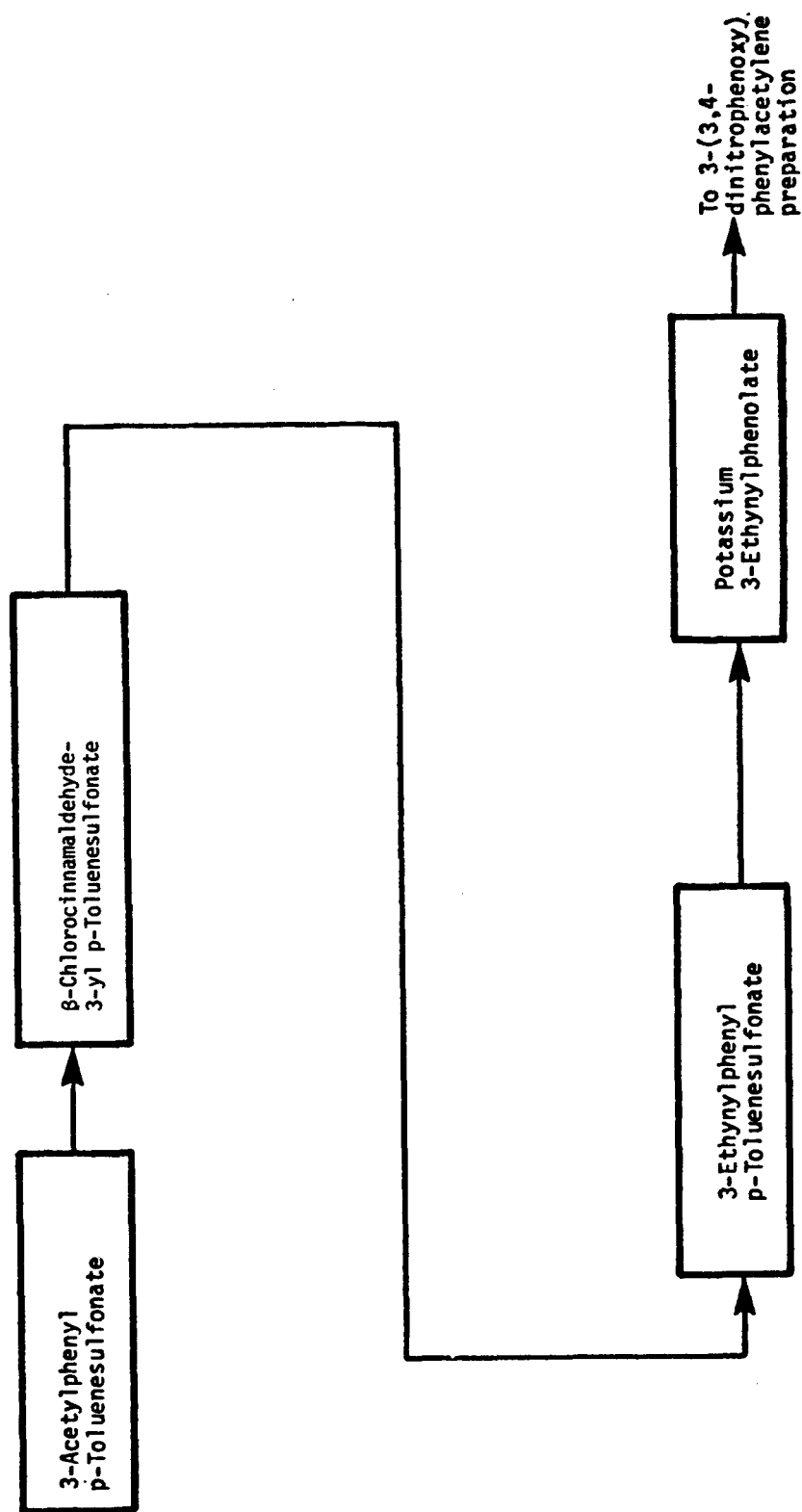
39

Figure 16. ATQ synthesis procedure summary.

40
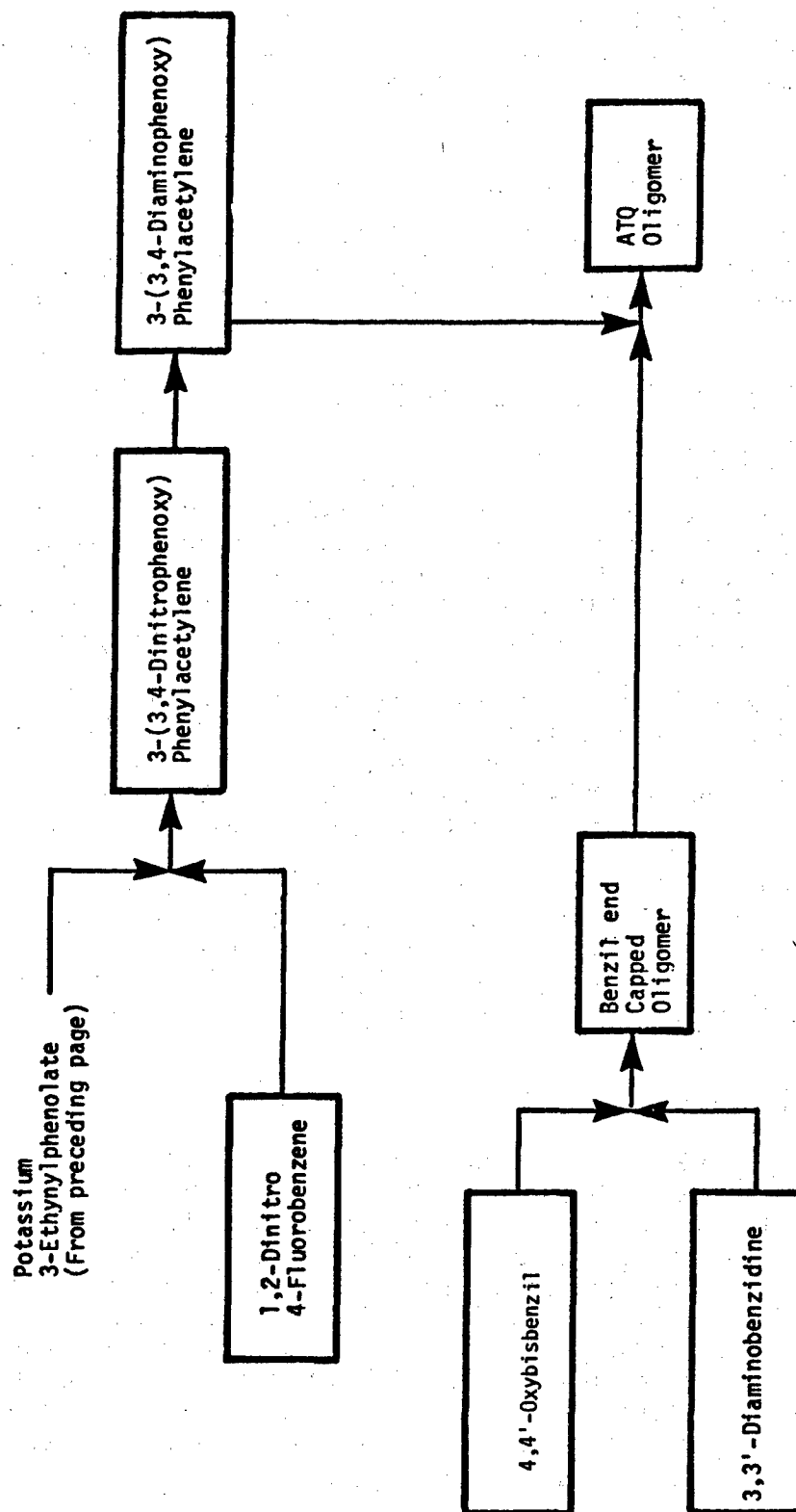
Figure 16. Concluded.

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Two batches of the ATQ oligomer were prepared by these procedures. Characterization data for these oligomer batches are provided below. A total of 196 grams of the intermediate 3-(3,4-dinitrophenoxy)phenylacetate were submitted to Dr. Fred Arnold at the Air Force Materials Laboratory. This concluded synthesis efforts for the first ATQ structure.

Prepolymer Characterization

Characterization data on the two batches of ATQ prepared during the course of this program are listed in Table 10. This data provided needed information on ATQ oligomer quality and its ability to be processed.

2.3.3 Prepreg and Composite Development

ATQ Solution Prepreg

A sample of ATQ oligomer (Batch JH-1-64) was used for solution prepregging efforts. Methylene chloride was selected as the solvent. This selection was made to continue work reported in the AFML evaluation of ATQ (Reference 9). Thornel 300 yarn (3000-filament count) was used as the reinforcement. Prepreg was produced on drum winding equipment.

After impregnation, a drying study was conducted at 220°F under vacuum. A 2-inch x 2-inch, single-ply prepreg sample was used in this study. Exposures of 30 and 60 minutes were used. No additional weight loss was obtained between the 30- and-60 minute exposures. Based on these results, the balance of the prepreg was dried for 30 minutes at 220°F under vacuum.

Good penetration of the Thornel 300 yarn was achieved. Resin content of the prepreg was 41.5 percent and the prepreg was tack free. The ATQ-Thornel 300 prepreg was, however, somewhat fragile since the ATQ polymer was powdery. This prepreg was used in the layup procedure development and the cure/laminate procedure development efforts described below.

ATQ Hot-Melt Prepreg

An initial assessment of the capability for hot-melt prepregging of the ATQ resin was completed. Batch JH-1-64 was used in the assessment. As discussed below, this resin batch first appeared to be unsuitable for hot-melt prepreg production. It now appears that higher temperatures than those described below need investigation before a final decision is made that ATQ is not hot-meltable. The approach used in this assessment was to first determine gel behavior of the resin. Determination of gel behavior was a significant indicator of the effects of heating on resin flow and viscosity. Next, films were prepared from the ATQ oligomer. The films were then placed over reinforcement fibers and pressure applied to assess suitability for prepregging.

Suitability of the ATQ batch for hot-melt prepreg application would have been indicated by complete reinforcement penetration by the resin, with

TABLE 10. ATQ OLIGOMER CHARACTERIZATION DATA

Batch Number	Batch Size (grams)	Tg^a (^oC)	PMT^b		Gel		IR Spectra
			Fusion	Melting	Temp.	Time	Benzil Peak Presence
			(^oC)	(^oC)	(^oC)	(sec)	
JH-1-60	45	315	180	215	214	228	None
JH-1-64	124	320	180	220	213	240	Trace

Batch Number	Volatiles		DSC Analysis^c			
	Temperature (^oC)	Weight Loss (Percent)	Exotherm Onset (^oC)	Exotherm Peak (^oC)	Exotherm Area (cm^2)	Sample Size (grams)
JH-1-60	300	0.3	178	230	45.2	0.028
JH-1-60	300	0.3	182	230	27.45	0.0247

[a]Glass transition temperature after 16 hours at 600°F

[b]Polymer melt temperature

[c]Differential scanning calorimeter, run at 5°C/min in nitrogen

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retention of adequate flow for composite curing. The gel time and viscosity behavior for ATQ Batch JH-1-64 were assessed by heating samples of the resin. The heated sample was manually probed at time increments to determine gel and viscosity behavior. Four temperatures were used -- 450°F, 425°F, 400°F, and 350°F. Times at which gel and viscosity were assessed ranged from 20 seconds to 15 minutes. Significant results included the following:

- At 450°F, softening began after 20 seconds. Viscosity had increased significantly after 210 seconds. After 240 seconds, the resin had hardened and the resin fractured when probed.

- At 425°F, initial melting occurred after 20 seconds. When probed, the viscosity was lower than the above 350°F sample. Hardening was complete after 8 minutes.

- At 350°F, no melting occurred until spatula-applied pressure was exerted. When heated to 400°F after 3 minutes at 350°F, melting occurred during the heat rise. Hardening was complete after 15 minutes total time.

Based upon the above results, effort was directed toward evaluating the film-forming characteristics of ATQ Batch JH-1-64. This was done by placing portions of the resin between release paper on a press platen. Heat and pressure were then applied. Sufficient pressure was applied to close the press platens to 0.016-inch shims.

The initial temperature used was 375°F. The resin sample was placed under contact pressure for 90 seconds. Pressure was then applied over a 15-second period to close the platens to the shims. The resulting disc-shaped film was continuous and appeared free of macroscopic defects such as voids or unmelted resin lumps. However, the resulting film was fragile and fractured easily.

This sample was then exposed to 450°F. This was done to verify that the resin would resoften and to determine the gel time. The ability to resoften was considered critical to use of hot-melt applied ATQ in composite curing. Similarly, a sufficient gel time would be required during composite curing to permit the resoftened resin to flow to provide an acceptable laminate. Resoftenilng of the film did occur, but gel occurred after only 3.5 minutes at 450°F.

Subsequent attempts at film preparation followed the procedures described above but with temperatures of 400°F, 425°F, and 450°F. All films were cooled under pressure. The best film was produced at 450°F.

Films prepared at 375°F and 450°F were then placed on Volan finished Style-181 glass fabric. Pressure was again applied at the same temperature used in forming the resin films. Inadequate fabric penetration was obtained at 375°F. Adequate penetration was obtained at 450°F. However, as previously noted, 450°F provided unacceptably short gel time for subsequent processing. Similar results were obtained with Thornel 300 and Celion 3000 graphite fibers.

In summary, hot-melt approaches for this oligomer did not appear feasible within the parameters discussed above. Temperatures as high as those investigated for Thermid 600 were not investigated in this study. Subsequent testing suggests that higher prepregging temperatures should be investigated. However, some quick-chill method would likely be required as was found necessary with Thermid 600.

Layup Procedure Development

The layup procedure for the initial ATQ laminate prepared from the solution prepreg paralleled that used for Thermid 600. As described in Section 2.2.3, this procedure used TX-1040 as a separator and Style-116 fiberglass as the bleeder. Layup of the laminate was accomplished with standard handling procedures. As discussed above, future efforts will use the lower cost (BATQ-H) resin system.

Cure/Laminate Procedure Development

Prepreg Batch 6-15 was used in the initial cure/laminate procedure development. As noted above, Prepreg Batch 6-15 used ATQ Batch JH-1-64 applied from methylene chloride solution to Thornel 300 unidirectional reinforcements.

Due to the limited quantity of ATQ available, the following technique was adopted to minimize material use. First, a tentative cure cycle was defined. This cure cycle was then evaluated on a two-ply layup of the dried ATQ prepreg. If, after cure, the two-ply layup was determined to be of acceptable quality, the same cure cycle was employed on a standard thickness layup. This approach minimized material use for determining, on a preliminary basis, the acceptability of a specific cure cycle.

A two-ply layup was completed using the procedures described above. The layup was placed in a thermocouple instrumented trap mold and cured by the following schedule:

1. Place mold in press preheated to 550°F

2. Hold under contact pressure for 1 minute

3. Apply 200 psi

4. Hold at 550°F under 200 psi for 2 hours

5. Cool under pressure to 150°F

Results for the initial two-ply laminate indicated the acceptability of the cure cycle. The laminate (6-15A) exhibited flow, excellent fiber wetting, and freedom from macroscopic voids.

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The procedures described above were used for Laminate 6-15B. Laminate 6-15B was 10-ply, 2-inch x 2-inch, with unidirectional ply orientation. Visual quality of this laminate was excellent. Laminate thickness was 0.074 to 0.076 inch. Specific gravity was 1.50. This specific gravity was sightly lower than that obtained for Thermid 600 Laminate 6-17B, as described in Section 2.2.3. Calculated resin content was 31.92 percent. Ten short beam shear specimens were machined from Laminate 6-15B. Four of the specimens and the unmachined portion of Laminate 6-15B were placed in a desiccator. The remaining six short beam shear specimens were then postcured for 16 hours at 600°F in air. Test results for these specimens are provided in Table 11.

The remaining section of Laminate 6-15B was postcured for 16 hours at 700°F in air. The section was then machined into short beam shear specimens and tested by the previously reported methods. One 700°F postcured specimen was tested at 350°F. Results are also reported in Table 11.

As shown in Table 11, no significant change in short beam shear strengths occurred as a result of either of the postcure conditions evaluated. This reflects the high thermal oxidative stability of the ATQ system.

2.3.4 Summary of ATQ Development Efforts

Virtual equivalence to the ATQ graphite composite properties reported by the AFML were obtained by our laboratories. Initially, hot-melt methods did not seem indicated for this polymer. The use of higher prepregging temperatures, however, is indicated. A more economically attractive ATQ structure (BATQ-H), discussed in the next section, has replaced the original ATQ structure.

2.4 LOW-COST ACETYLENE-TERMINATED QUINOXALINES (BATQ-H)

Use of acetylene-terminated quinoxaline as the matrix for advanced composites in hardware applications required development of a lower-cost oligomer. The first ATQ structure used in the early portion of this program has been reviewed in the previous section. A most attractive approach to lower-cost ATQ oligomers is the development of simplified synthesis routes to the intermediates used to prepare ATQ oligomers.

The objective of the effort is to develop a low-cost synthesis for the Benzil end-capped Acetylene-Terminated Quinoxaline-Hydroquinone (BATQ-H) oligomer. The currently used synthesis route is shown in Figure 17.

The key intermediates for the BATQ-H oligomer synthesis are 3-ethynylphenol and 4-nitrobenzil. The 4-nitrobenzil is required for synthesis of both the benzil end-capping molecule and the bis-α-diketone, 1,4-bis(4-benziloxy)benzene. Low-cost synthesis studies for both of these compounds currently underway are discussed below. Experimental procedures are provided in Appendix B.

TABLE 11. ATQ LAMINATE TEST RESULTS

Laminate Identity	Postcure	Specimen Number	Test Temperature (^{0}F)	Shear Strength (ksi)
6-15B	--	1	70	13.8
	--	6	70	13.5
				———
				13.6 Avg
	--	2	450	6.9
	--	4	450	6.7
				———
				6.8 Avg
	a	3	70	14.5
	a	7	70	14.0
	a	10	70	14.0
				———
				14.1 Avg
	a	5	450	7.2
	a	8	450	7.0
	a	11	450	7.4
				———
				7.2 Avg
	b	12	70	13.8
	b	15	70	13.7
				———
				13.8 Avg
	b	16	350	9.1
	b	13	450	7.5
	b	14	450	7.4
				———
				7.5 Avg

[a] 16 hours at 600^{0}F in air
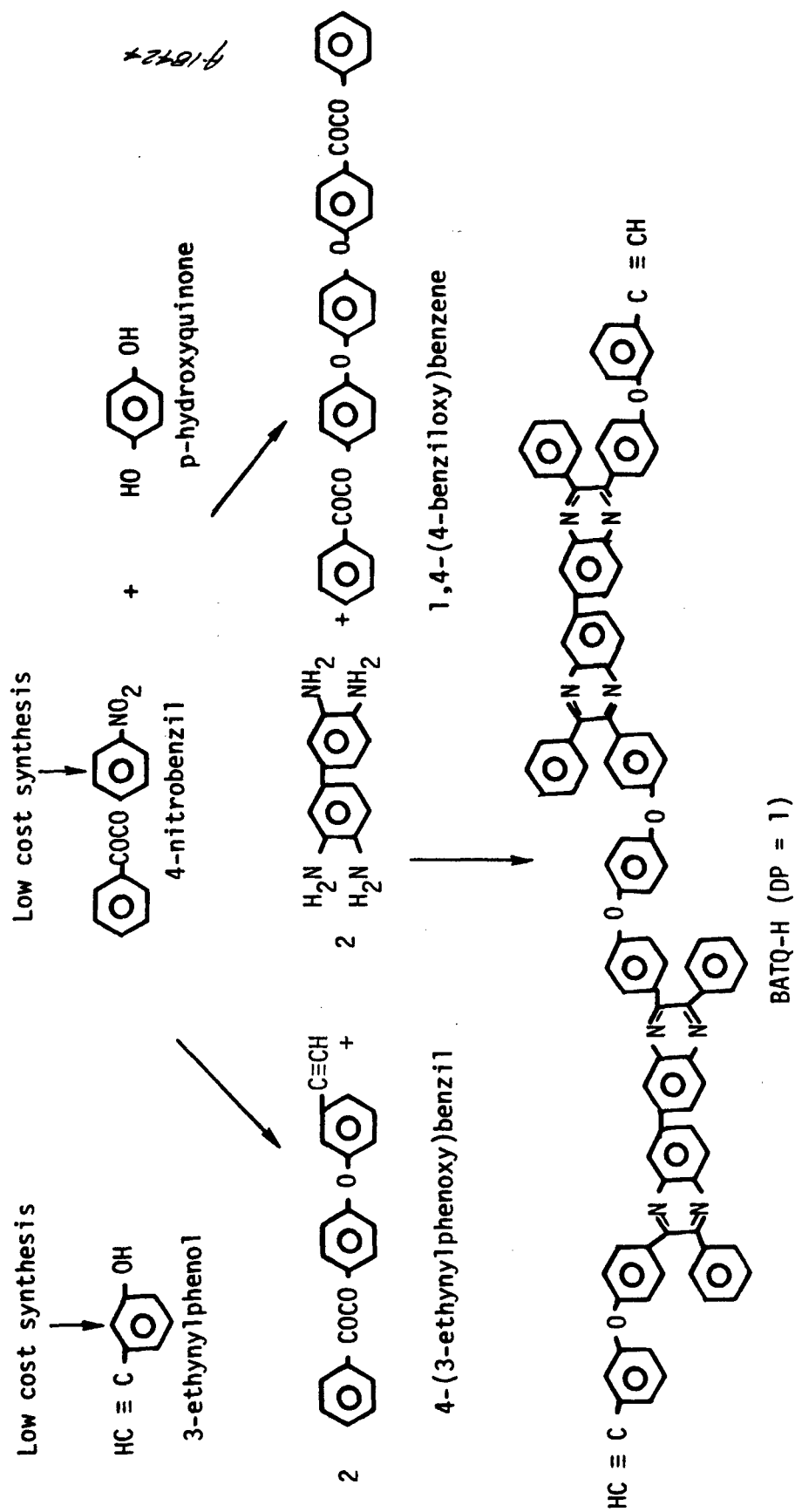
[b] 16 hours at 700^{0}F in air

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Figure 17. Low cost synthesis of BATQ-H.

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2.4.1 4-Nitrobenzil

Two preparations of 4-nitrobenzil have been completed following the procedure of Womack, Campbell, and Dodds (Reference 10). Yields have averaged 35 percent for the acylation-nitration and 92 percent for hydrolysis oxidation (Reference 11).

An attempt to simplify the above two-step synthesis was attempted. The simplification was intended to avoid isolating and purifying the 4'-nitrobenzoin acetate prior to oxidizing with nitric acid. The 4-nitrobenzil was definitely produced in the reaction. However, isolation from the side products (among which are benzoic acid and -nitrobenzoic acid) has not been resolved to the point that this modification would prove beneficial.

2.4.2 1,4-Bis(4-benziloxy) Benzene

One preparation of bis- -diketone was completed using the procedure of Arnold (Reference 12). This resulted in the isolation of 5.9 grams of lemon-yellow crystals as described in Appendix B. Further preparations of this bis- -diketone will be undertaken as required.

2.4.3 3-Ethynylphenol

Attempts to prepare the title compound directly by treating m-hydroxy acetophenone with DMF/POCl$_3$ followed by treatment with base are under investigation. Conditions employing a greater-than-calculated stoichiometric quantity of phosphorus oxychloride have led to the isolation of a yellow solid of unknown composition. Attempts are underway to purify and identify this material.

Two promising alternate routes scheduled for investigation are elimination of triflic acid (Reference 13) and a "low cost" direct synthesis via a Wittig intermediate (Reference 14).

2.4.4 BATQ-H Hot-Melt Feasibility Investigation

Hot-melt prepreg feasibility investigations were conducted on the lower-cost Benzil end-capped Acetylene-Terminated Quinoxaline-Hydroquinone (BATQ-H) oligomer. These efforts focused on defining the gel time and flow properties of a BATQ-H sample obtained from Dr. F. Arnold of the AFML.

Figure 18 compares the gel times of the BATQ-H sample and an ATQ sample from Batch JH-1-64 (average of five determinations for each point shown). BATQ-H provides a slightly longer gel time throughout the entire range of temperatures examined. As noted for Thermid 600, a very easily observed transition from molten polymer to rubbery polymer is seen at the higher temperatures.

Since the gel point determinations at the higher temperatures appeared accurate and the expected semilog relationships were obtained, comparison of
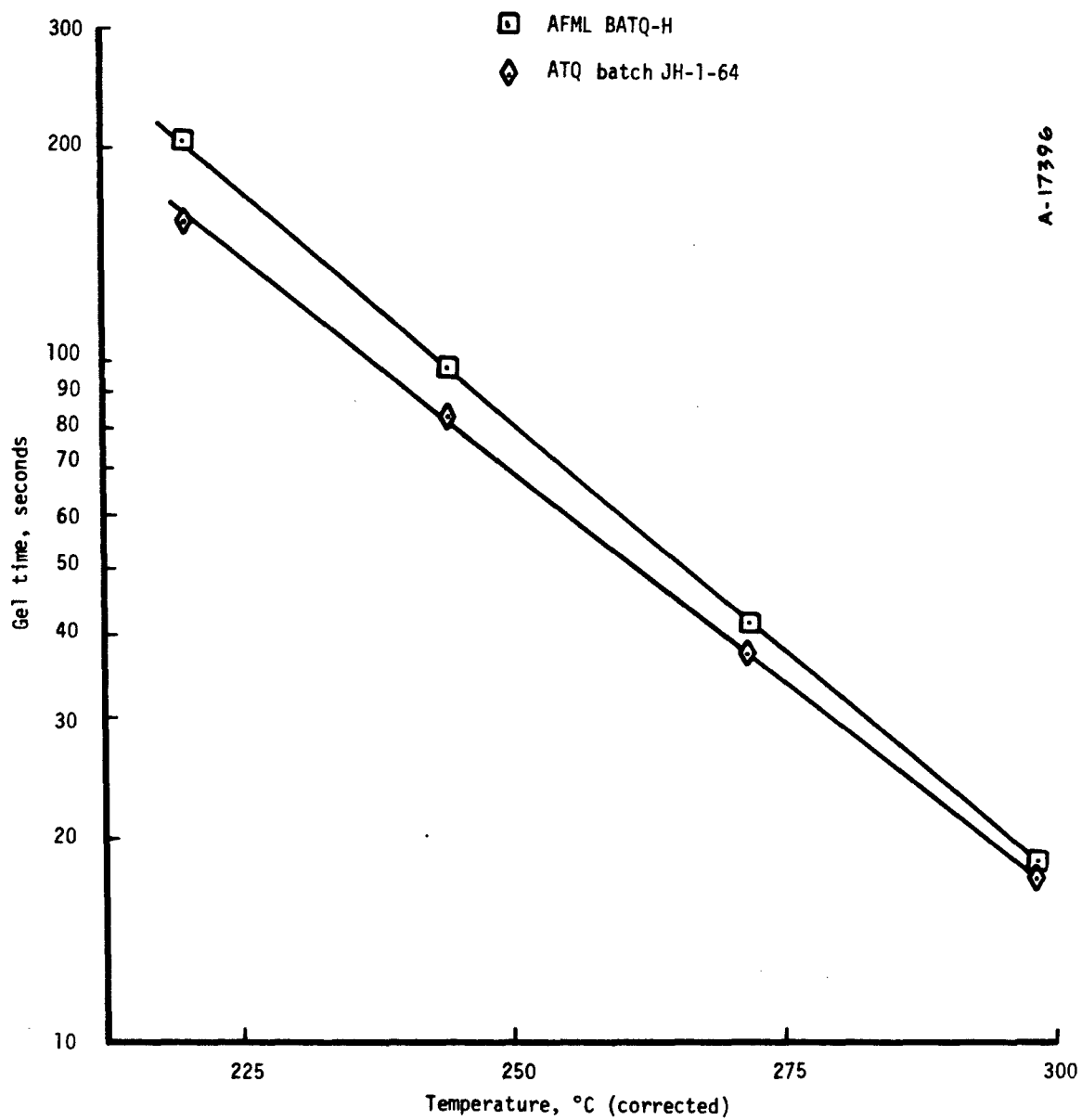
Figure 18. Gel times of ATQ and BATQ-H.

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the gel times of four Thermid 600 batches to the gel times of the two ATQ's was conducted. As shown in Figure 19, the ATQ and BATQ-H polymers have a slightly different slope from the Thermid polymers. Since the measured gel times are the result of the reaction rate in the systems, gel should occur at approximately the same degree of polymerization. It is tentatively concluded that only slight differences exist in the relative reactivity of the two ATQ systems and the Thermid 600 system.

The slightly different slopes do point to some differences between the resins. At 300°C, ATQ and BATQ-H have 50 percent again as much gel time as the Thermid 600. This suggests that a lower percentage of high-temperature gel time loss would be experienced with the quinoxalines than with the polyimides at 300°C prepregging temperatures (assuming equivalent prepreg qualities were obtained).

At 225°C, however, the ATQ sample had the shortest gel time of the samples tested. The gel time of the BATQ-H sample was about the same as the two Thermid samples that could be measured at this temperature. It should be noted that the Thermid 600 sample, LS7173, possessing the long gel time at 225°C, was prepared in m-cresol-dimethylformamide. The three other Thermid 600 resin samples shown in Figure 19 were prepared in N-methylpyrrolidinone.

The data contradicts the earlier conclusion that ATQ is not hot-melt processable. The data suggests that both ATQ and BATQ-H should be more amenable to hot-melt processing than Thermid 600 at high temperatures. This thesis appears substantiated by the film characterization efforts described below.

Flow characterisics of both ATQ oligomers were evaluated by Aerotherm's previously described pressout technique. Thermid 600 (Batch 6L606) was used as a standard for comparative flow property demonstrations of the ATQ oligomers. The technique used to compare the polymers was as follows: The press was preheated to the test temperature. After it had stabilized, all three polymers were pressed out, one after the other, as rapidly as possible. The Thermid 600 sample was used as a standard for comparison of the relative flow properties of the ATQ system as shown in Figure 20. The lack of linear pressout diameter with increasing temperature is likely due to one of the pressout temperatures being slightly in error. (Comparison to Figure 9 suggests that the 225°C temperature may have been closer to 235°C, based on the Thermid pressout diameter obtained.)

Even though the quinoxalines provided smaller diameter pressouts than Thermid at 275°C, this difference may not be found to be significant in actual prepregging operations at 275°C. The flow of both ATQ's at 225°C appears to be in excess of the Thermid sample, suggesting better processability of the prepreg product at that temperature.

2.4.5 Summary of Low-Cost Acetylene-Terminated Quinoxalines (BATQ-H)

Promising new synthesis routes to BATQ-H intermediates have been identified and efforts to investigate these routes are in progress. Of particular interest is the low-cost synthesis of 3-ethynylphenol.
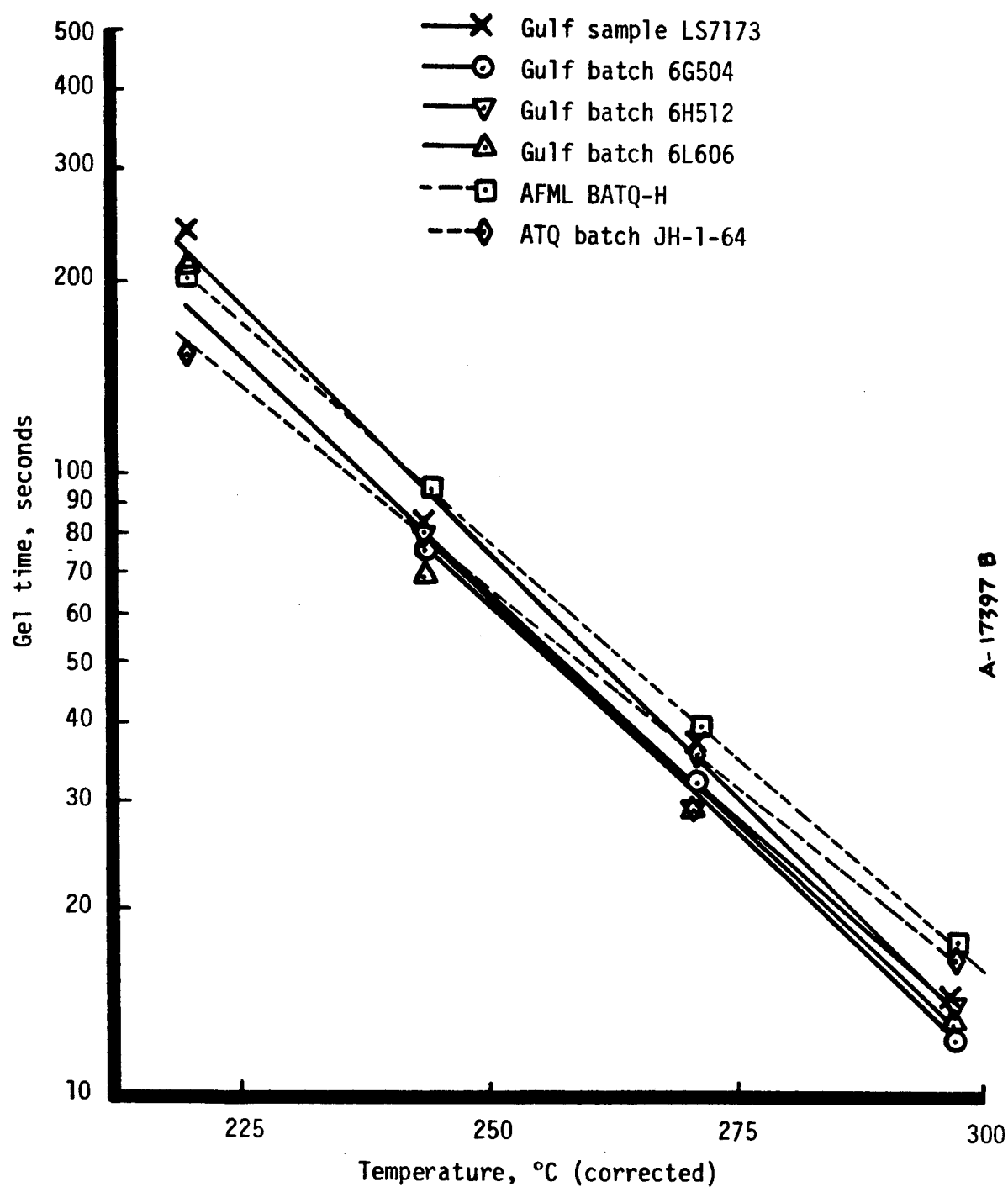
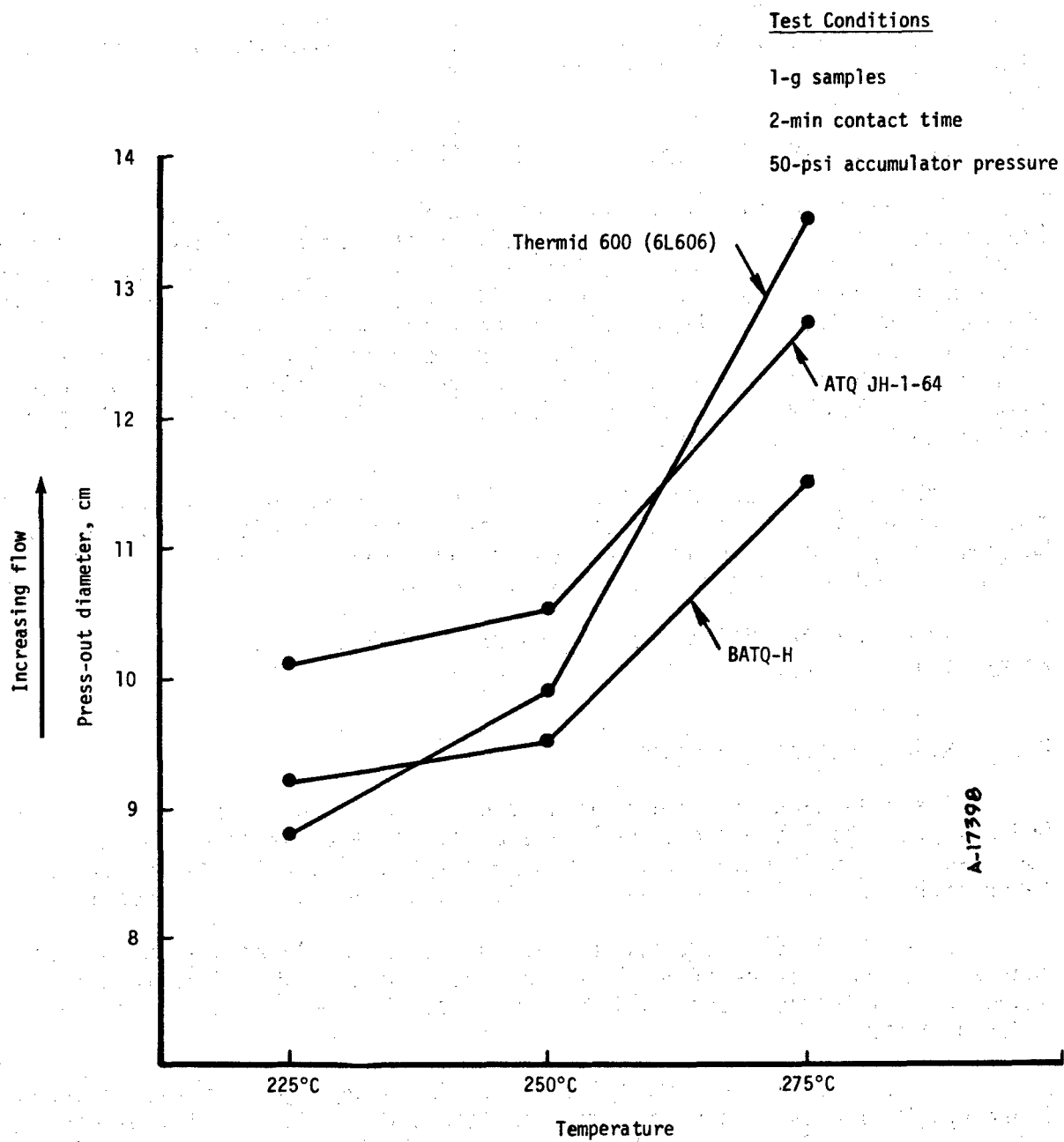Figure 19. Gel time versus temperatures for Thermid, ATQ and BATQ-H.

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Figure 20. Press-outs of ATQ, BATQ-H and Thermid 600.

The gel times and melt-flow properties of the acetylene-terminated polyimides and the acetylene-terminated quinoxalines have been found to be approximately equivalent.

The facile solubility of the quinoxaline systems may offer some real advantages to the processing of these systems.

2.5   POLYIMIDAZOQUINAZOLINE (PIQ) DEVELOPMENT

Polyimidazoquinazolines -- developed for the Air Force by Aerotherm (Reference 16) -- are a condensation resin system which releases phenol and water when cured. The high cure (875°F) and performance temperatures of PIQ are near the upper limits of fiber stabilities. Initial investigations with PIQ were conducted with Modmor II, the most thermal-oxidatively stable HTS fiber known at that time. Today, however, emerging graphite fabrics are considered the best form of reinforcement for very brittle PIQ prepolymers. Furthermore, Modmor II is not available in less than 10,000 filaments per tow, which limits its weaveability.

Fabrics also require a surface finish -- or sizing -- to prevent fiber damage during the weaving operation. These sizings, typically epoxies, can be removed by heat cleaning. The heat-cleaned fabrics can then be used "as is" or resized with a more thermally stable sizing.

In making the PIQ composites described below, state-of-the-art reinforcements and sizings have been used.

2.5.1   Reinforcement Selection

The selection of reinforcement fibers for the high-temperature AF-R-553(80) prepreg, layup and cure/laminate development was based on three factors: (1) anticipated composite cure temperature, (2) anticipated use temperature, and (3) experience with alternate forms of reinforcement.

Prior AF-R-553(80) composite evaluation work (Reference 15) showed that a cure temperature of 875°F is required for AF-R-553(80) composites. Based on this earlier work, AF-R-553(80) laminates were slated to be cured under nitrogen.

As reported in Section 2.2.1, most fibers undergo significant graphite fiber weight losses in air environments at 550°F and 700°F. In the work cited in Section 2.2.1, only GY-70, Hercules HM/PVA (3K), and Modmor II retained a high percentage of their original weights after exposure to the high-temperature air environment.

Since AF-R-553(80) graphite composites would actually be used in high-temperature air environments, the thermal oxidative stability of the fiber remained critically important. The prior work (Reference 15) provided AF-R-553(80) -- Modmor II composite weight loss data in high-temperature air environments. This data, however, did not extend beyond 200 hours at 700°F.

Based on experience with both unidirectional tape and woven fabric reinforcement forms, all available fiber data generated were reviewed in detail. As noted above, when the initial PIQ reinforcement was selected, GY-70, HM/PVA (3K), and Modmor II fibers showed the highest thermal oxidative stability. GY-70 fiber was evaluated in the surface-treated single-end form. However, this fiber has not been widely used, due mainly to its very high modulus and the comparatively high cost of the single-end fiber. The high modulus makes the fiber brittle, so that it requires careful handling through all stages of prepreg production and use to prevent composite degradation. Although GY-70 multiend tape costs less than GY-70 fiber, brittleness is still a problem. Furthermore, the use of GY-70 would be limited to unidirectional tape prepreg products.

Data on the 3000-filament-count Hercules HM/PVA indicated that it could be handled routinely and would be applicable to both unidirectional-tape and woven-fabric product forms. However, lack of surface treatment and matrix-compatible finishes would limit the structural efficiency of the fiber in composite applications.

The Modmor II fiber proved to have many potential advantages. Modmor has mechanical properties typical of graphite fibers which have been widely used in structural composite applications. In addition, its cost is reasonable, and it has been used on a limited basis with AF-R-553(80) matrix resin. The 10,000-filament-count tow form of Modmor II, however, is limited to the unidirectional tape prepreg product form.

As noted in Section 2.2, as part of the AF-R-553(80) reinforcement selection, a limited survey was conducted to identify newer fibers with mechanical properties approximating those of Thornel 300 and improved oxidative stability. During this survey, Celanese announced the Celion 3000 fiber. This fiber was reported to have the following characteristics:

- Mechanical properties essentially equal to Thornel 300

- Higher thermal-oxidative stability than Thornel 300

- Availability in either surface treated or surface treated with epoxy

- Three-thousand-filament-count tows

Discussions with Celanese indicated that the fiber was available in only limited quantities. Although Celion 3000 appeared to offer a number of advantages -- particularly its applicability to both tape and woven fabric prepreg forms -- including the fiber in this program was considered premature without confirming its thermal oxidative stability and verifying its structural performance capability.

Although confirmation of Celion 3000 thermal oxidative stability is still in progress, the structural performance capability of the fiber has been evaluated on an epoxy-sized Celion 3000 woven fabric. This fabric fabric was produced by the Woven Structures division of Hitco. The weave construction was 24-inch x 23-inch, eight-harness satin. A state-of-the-art

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epoxy matrix was selected for initial characterization so that structural capability of the fiber and fabric could be evaluated.

A small prepreg batch of the Celion 3000 epoxy-sized fabric was impregnated with an epoxy resin using the same formulation as the the extended flow-life resin developed for the Air Force by Aerotherm (Reference 16). The resulting epoxy-graphite fabric prepreg was fabricated into a 4-inch x 4-inch, 0.080-inch thick, six-ply composite. When the prepreg and laminate were inspected, it was clear that neither was optimum. However, since optimization was clearly not warranted under this program, the decision was made to perform limited composite testing of the material.

The results of short-beam shear and flexure tests shown in Table 12 confirmed the excellent structural performance of the Celion 3000 fabric. Reinforcement construction was taken into account in assessing these test results. The most significant aspect of reinforcement construction was that in the 24-inch x 23-inch fabric form, only about 50 percent of the reinforcement volume fraction was aligned in the test direction. Given this fact, the shear and flexure data presented in Table 12 are consistent with expected values.

Prior to initial AF-R-553(80) prepreg procedure development efforts, additional Celion 3000 reinforcement was received. This reinforcement was the same 24-inch x 23-inch, eight-harness satin-woven fabric form. But unlike the previous sample, it had been heat-cleaned after weaving to remove the epoxy sizing.

Since the stability of the epoxy sizing and the initial Celion fabric during AF-R-553(80) processing had been of concern this heat-cleaned fabric was selected as the reinforcement for the initial AF-R-553(80) prepreg development effort. An unsized reinforcement was considered acceptable, since Modmor II with no sizing was used in the previous work.

2.5.2 PIQ Synthesis and Characterization

Synthesis

The synthesis of AF-R-553(80) PIQ is summarized in Figure 21. Experimental procedures used for the following preparations are provided in Appendix C.

- 4,4'-bisbenzoic acid (two methods)

- Diphenyl sulfite

- Diphenyl 4,4'-bisbenzoate

- Purification of 3,3'-diaminobenzidine (DAB)

- AF-R-553(80) prepolymer synthesis

TABLE 12. CELION 3000 WOVEN FABRIC COMPOSITE DATA[a]

Specimen Number	Test Temperature (°F)	Flexure Strength (10^3 x psi)	Flexure Modulus (10^6 x psi)	Short Beam Shear Strength (10^3 x psi)
1	70	109	10.7	8800
3	70	134	10.6	7710
		——	——	——
	Avg	124	10.6	8255
2	350	105	11.1	7080
4	350	105	10.6	6880
		——	——	——
	Avg	105	10.8	6980

[a]Six-ply epoxy sized Celion 3000/epoxy matrix composite
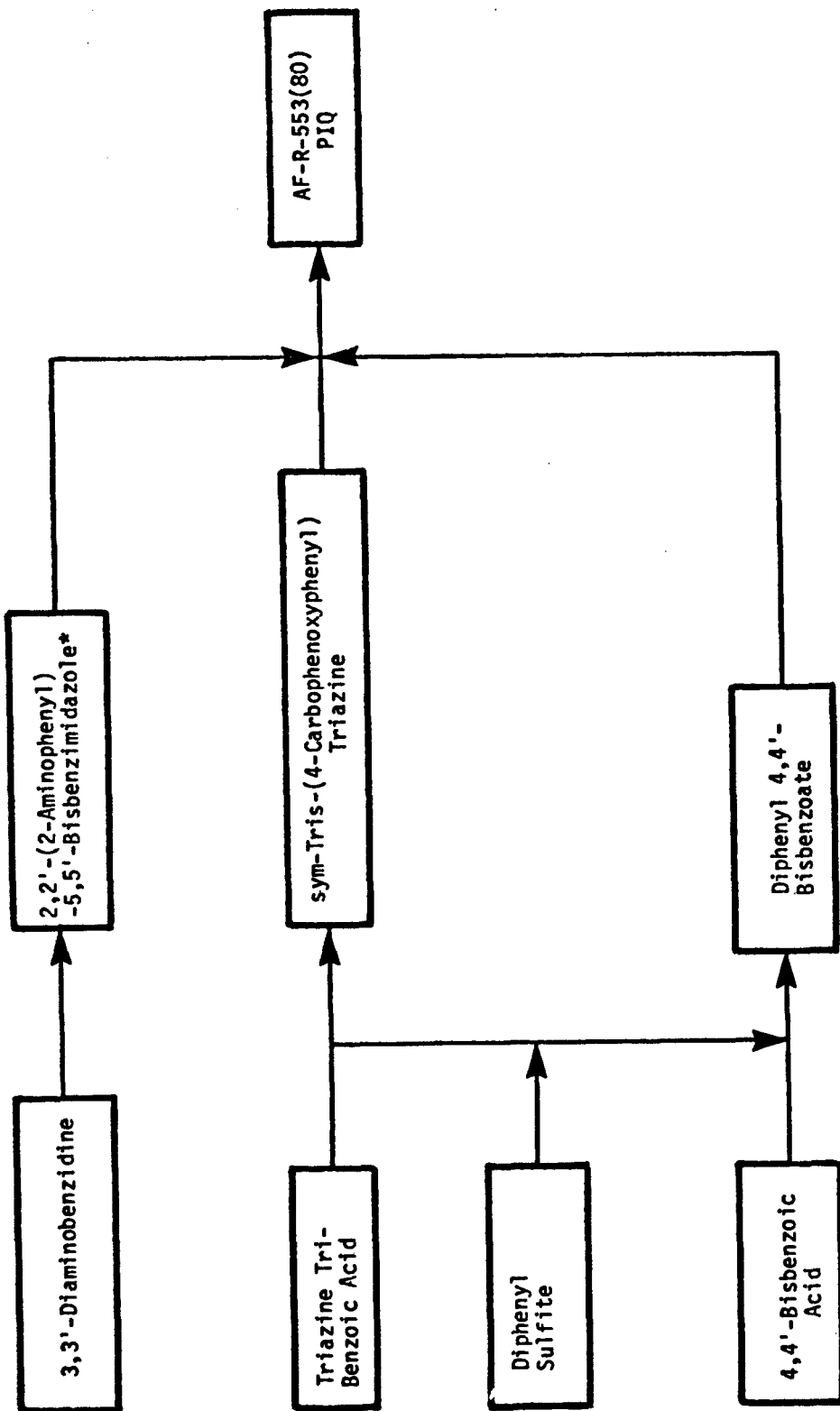
Figure 21. AF-R-553(80) PIQ synthesis procedure summary.

The flow chart contains the following boxes and labels:

- 3,3'-Diaminobenzidine
- 2,2'-(2-Aminophenyl)-5,5'-Bisbenzimidazole*
- Triazine Tri-Benzoic Acid
- sym-Tris-(4-Carbophenoxyphenyl) Triazine
- Diphenyl Sulfite
- 4,4'-Bisbenzoic Acid
- Diphenyl 4,4'-Bisbenzoate
- AF-R-553(80) PIQ

*AF-R-500 Amine

Prepolymer Characterization

An initial batch (RJM-2-59) of AF-R-553(80) PIQ was synthesized and preliminary characterization data developed. Characterization tests conducted for this batch were limited to those parameters determined to be most critical from prior work (Reference 16).

Characterization data on Batch RJM-2-59 is summarized in Table 13.

TABLE 13. AF-R-553(80) PIQ CHARACTERIZATION DATA FOR BATCH RJM-2-59

Parameter	Value
Batch size	200.8 grams
Polymer melting point	183°C - 188°C
Volatiles[a]	19 percent
[a]Run at 875°F, 1-hour exposure	

2.5.3 Prepreg and Composite Development

Prepolymer Batch RJM-2-59 was used for the prepreg and composite development efforts. When the prepreg techniques to be used were assessed, the common denominator for prior AF-R-553(80) work was found to be the solvent NMP. Solvents are typically used to permit the resin to be applied to the reinforcement. However, the presence of solvents in prepregs complicates the composite cure cycle, and degraded composite properties can result if the residual solvent causes porosity in the cured laminate.

As noted in Table 13, the polymer melt temperature for Batch RJM-2-59 was reported to be 183°C to 188°C. Although this temperature is high for conventional hot-melt prepreg equipment and procedures, Aerotherm's special hot-melt equipment made it possible to evaluate the feasibility of prepregging the AF-R-553(80) resin by hot-melt techniques.

For this feasiblity evaluation, AF-R-553(80) resin was applied to the heat-cleaned Celion 3000 fabric using hot-melt techniques. Hot-melt prepregging was accomplished by coating each side of the fabric in separate passes. Resin was applied to the fabric using a doctor blade with a 0.020-inch gap setting. Resin pickup was 53 percent. The resin appeared to have penetrated the Celion 3000 fiber bundles. Sufficient prepreg was produced to permit layup and cure/laminate development on small-scale composites.

Layup Procedure Development

The layup procedure for the initial work on AF-R-553(80)-woven Celion 3000 paralleled that previously used for Thermid 600 and ATQ. Porous teflon-coated fiberglass cloth (TX-1040) was used as the separator. Style 116 fiberglass was selected as the bleeder.

These separator and bleeder materials were selected since, based upon prior AF-R-553(80) work, the anticipated cure cycle (described below) would avoid exposure of the TX-1040 to temperatures which could cause its decomposition or have detrimental effects on the laminate. If successful, the approach would offer the potential for using standard shop supplies in fabricating high-temperature resin matrix composites. This would make acceptance of the AF-R-553(80) resin-based prepregs by airframe manufacturers a more realizable goal.

Layup of the heat-cleaned Celion 3000 fabric reinforced AF-R-553(80) prepreg was accomplished using standard handling procedures.

Cure/Laminate Procedure Development

The initial evaluation of AF-R-553(80) cure/laminate had two objectives: (1) to assess the feasibility of using standard shop materials in the layup, and (2) to verify the cure cycle. The approach taken for the initial laminate was to expose standard shop materials to temperatures no higher than 650°F. After this cure, the laminate would be removed from the mold and the standard shop materials removed. Cure of the laminate would then be completed at 875°F. This approach paralleled that used in previous programs.

AF-R-553(80) cure/laminate procedure development began with Prepreg Batch 11-1. The layup was placed in a 4-inch x 2-inch trap mold. A thermocouple was placed in the layup and the mold bagged in aluminum foil. The following cure cycle was then performed under a nitrogen atmosphere:

1. Preheat press to 650°F

2. Load foil-bagged mold into preheated press

3. Apply contact pressure

4. Hold 10 minutes under contact pressure after mold reaches 650°F

5. Apply 100 psi

6. Hold at 650°F under 100 psi for 120 minutes

7. Cool under pressure in nitrogen

When the layup was removed from the cooled mold, effort on this laminate was terminated, since no evidence of interply adhesion was observed.

Subsequently, although four additional attempts were made to produce an acceptable AF-R-553(80)/Celion 3000 laminate, none of the cure modifications attempted provided a high-quality material. Table 14 provides a summary of these four attempts to achieve an acceptable laminate. As the table shows, the most common problem was failure to achieve sufficient resin flow and/or ply-to-ply adhesion due to poor adhesion of PIQ to the fiber.

After the experiments described above, additional information became available on heat-cleaned Celion 3000 fabric which indicated that heat cleaning had been performed at too high a temperature. As a result, significantly lower than expected composite shear strengths were obtained. Thus, the condition of the surface of the Celion 3000 was a possible cause for not obtaining high-quality PIQ laminates.

2.5.4 Summary of PIQ Development

In the early development of the PIQ resin matrix, Modmor II was the only reinforcement fiber considered. During the present program, Celion 3000 was identified as a fiber with equivalent thermal oxidative stability. However, experiments with heat-cleaned Celion 3000 fabric with PIQ showed that the material does not provide the strength required. In addition, surface finish problems are indicated, even though the PIQ matrix was applied to the reinforcement by hot-melt methods rather than by the solvent (NMP) impregnaton used for earlier tests. Accordingly, future tests with PIQ and Celion must address the fiber surface finish.

TABLE 14. AF-R-553(80) LAMINATE ATTEMPTS WITH HEAT-CLEANED CELION 3000
FABRIC

Laminate Identity	Cure Condition	Results
11-2	• Layup placed in unheated press, heated to 650°F in 55 minutes • 100 psi applied after 5 minutes, 650°F hold	Marginal flow; porous laminate edges and surface resoftened during postcure
11-3	• Same as 11-2 except 200 psi applied after 5 minutes, 650°F hold	Porous appearance; edges delaminated during removal from mold
11-6	• 200 psi applied after 15 minutes, 650°F hold • 850°F, 2-hour cure performed without removal from mold • Cooled to 500°F before removal from press	Laminate resin starved; matrix porous
11-7	• Same as 11-6 except 650°F reached after 30 minutes	No ply-to-ply adhesion

APPENDIX A

ATQ EXPERIMENTAL PROCEDURES

4,4'-OXYBISBENZIL

A mixture of diphenyl ether (68.2 grams, 0.4 mole) and phenylacetyl chloride (123.2 grams, 0.8 mole) was added dropwise to a slurry of aluminum chloride in methylene chloride. The temperature was maintained at 10^oC during the addition. Addition was complete after 1 hour and the mixture was allowed to warm to room temperature. The contents of the flask were then slowly added to a HCl-ice mixture. White crystals formed. The crystals were isolated, washed with a 5-percent sodium hydroxide solution, water, and finally ethyl alcohol. Recrystallization from toluene produced 127 grams (0.31 mole, 78-percent yield) of 4,4'bis(phenylacetyl)diphenyl ether, melting point 166^oC to 167^oC.

This 4,4'bis(phenylacetyl)diphenyl ether was then oxidized with an excess of selenium dioxide (69.4 grams, 0.65 mole) in 500 ml of acetic acid. The mixture was stirred under reflux for 16 hours, at which time charcoal was added. The mixture was then filtered through a Celite cake. After cooling, the hot filtrate yielded 110.5 grams of yellow crystals. One recrystallization from isopropyl alcohol gave 100 grams, 74.6 percent, 4,4'-oxybisbenzil melting point 103^oC to 107^oC.

3,4-DINITROFLUOROBENZENE

Concentrated sulfuric acid (760 ml) was added dropwise to concentrated nitric acid (760 ml). The temperature was kept at 20^oC during the addition. After addition was complete, the mixture was warmed to 50^oC, and 1-nitro-3-fluorobenzene (141 grams, 1 mole) was added dropwise. The temperature was maintained between 55^oC and 60^oC. After the mixture had stood for an additional hour at 50^oC, it was poured into 4 liters of cracked ice. The yellow precipitate was washed thoroughly with water, a sodium bicarbonate solution, and again with water. The product was recrystallized twice from 95 percent ethyl alcohol. The yield was 109 grams (59 percent) of 3,4-dinitrofluorobenzene with a melting range of 49^oC to 50^oC.

β-CHLOROCINNAMALEDHYDE-3YL p-TOLUENESULFONATE

A 3-liter, three-necked flask equipped with a thermometer, nitrogen inlet, and addition funnel was dried for 3 hours at 100°F and purged with nitrogen. Dry N,N-dimethylformamide (500 milliliters) was added to the flask. The flask was then cooled to 20°C. Phosphorous oxychloride (153 grams, 1.0 mole) was added to the flask dropwise under nitrogen while the solution was stirred rapidly to maintain the temperature between 20°C and 25°C. After addition was complete, the solution was stirred at room temperature for 1 hour. At this point, dry 3-acetylphenyl p-toluenesulfonate (150 grams, 0.52 mole) was added to the dark-red reaction mixture and the solution stirred under nitrogen at 60°C for 3 hours. The contents of the flask were poured into a 4-liter beaker of ice water. Sodium bicarbonate was added to the stirred solution until foaming ceased. A dark, thick oily suspension resulted. The oil was extracted with methylene chloride. After evaporation of the solvent, the crude product was used without further purification in the preparation of 3-ethynylphenyl p-toluenesulfonate below.

3-ETHYNYLPHENYL p-TOLUENESULFONATE

Sodium hydroxide (34 grams, 0.85 mole), water (1800 ml) and p-dioxane (1200 ml) were added to a 5-liter round-bottomed, three-neck flask equipped with stirrer, condenser and thermometer. The mixture was stirred rapidly and heated to 80°C. Crude β-chlorocinnamaldehyde-3-yl p-toluenesulfonate (150 grams, 0.44 mole) was then added. The resulting mixture was stirred at 80°C for 15 minutes, at which time the flask was cooled in ice to room temperature. The contents of the flask were then transferred to a large separatory funnel and extracted with methylene chloride. The aqueous layer was saved for recovery of small amounts of 3-hydroxyphenylacetylene. The combined methylene chloride extracts were washed with 1N sulfuric acid and deionized water. The organic layer was then separated and evaporated to dryness, yielding crude product as a dark oil. Attempts to solidify the material by triturating in ice water were unsuccessful.

The hydroxy compound was recovered from the aqueous layer and retosylated to yield a dark oil, which was combined with the crude product. Chromatography on silica gel eluting with 1:1 hexane-methylene chloride yielded 12 grams of a dark-yellow solid, and a dark oil. The product is present in both fractions as indicated by the appearance of terminal acetylene C-H absorption at 3300 cm^{-1}. The solid was identified as β-chlorocinnamaldehyde-3-yl p-toluenesulfonate.

3-(3,4-DINITROPHENOXY)PHENYLACETYLENE

Potassium hydroxide (61.6 grams, 1.1 mole) was dissolved in 1 liter absolute methanol over a steam bath. Next, 3-ethynylphenyl p-toluenesulfonate (150 grams, 0.55 mole) was added, and the solution was heated to reflux for 1/2 hour. The methanol was then removed by distillation. At this time, dry benzene (300 ml) was added and distillation was continued until the residue approached dryness. The remaining benzene was removed by evaporation under vacuum. Pyridine (1200 ml) was added to the

potassium salts under nitrogen. The flask was cooled to 0°C and solid 3,4-dinitro-fluorobenzene (102 grams, 0.55 mole) was added. The mixture was stirred at room temperature for 1/2 hour and then at 40°C for 1 hour, at which time it was added to 2 liters of ice-cold 1N sulfuric acid and extracted with three 300-ml portions of methylene chloride. The extracts were washed with four 500-ml portions of 1N sulfuric acid and then with four 500-ml portions of water. The organic layer was rotary-solvent evaporated to a volume of 200 ml and filtered through a 2-inch x 6-inch dry column of silica gel. Methylene chloride was used to elute the product. Rotary-solvent evaporation of the methylene chloride eluate yielded 120 grams of yellow oil which solidified upon standing. The solid was recrystallized twice from methanol to produce 80 grams (47 percent) of 3-(3,4-dinitrophenoxy)phenylacetylene, melting point 75°C (DSC).

BENZIL END-CAPPED QUINOXALINE OLIGOMER

To a rapidly stirred solution of m-cresol (400 ml), 4,4'-bis(phenylgloxyaloyl)diphenyl ether (84.7 grams, 0.195 mole) and acetic acid (5 ml) under nitrogen were added dropwise to a solution of 3,3'-diaminobenzidine (20.8 grams, 0.097 mole) in m-cresol (400 ml). The tetraamine was dissolved by heating on a hot plate before being added. After the addition, the reaction mixture was stirred at room temperature for 2 hours, at which time distilling apparatus was attached and a 400-ml portion of m-cresol was distilled. The IR spectrum exhibited strong absorption at 1678 cm^{-1} for the diketone carbonyl groups.

3-(3,4-DIAMINOPHENOXY)PHENYLACETYLENE

Sodium dithionite ($Na_2S_2O_4$) (230 grams, 1.32 mole) and water (750 ml) were added to each of two 4-liter Erlenmeyer flasks equipped with magnetic stirrer. The sodium dithionite was dissolved by heating to 60°C. Then, a solution containing sodium hydroxide (52 grams, 1.3 mole) dissolved in water was added to each flask. Meanwhile, 3-(3,4-dinitrophenoxy)phenylacetylene (37.5 grams, 0.132 mole) was dissolved in methanol (750 ml) by heating. The hot methanol solution was then added quickly to the rapidly stirred solution of dithionite, and the flask was rinsed with methanol. A dark purple color formed immediately, which slowly changed to yellow, and then to milky white. Most of the methanol was then removed from the reaction solution in vacuo on a rotary evaporator; the temperature was maintained below 60°C. After removal of the methanol, the aqueous white suspension of end-capping reagent was cooled to room temperature and transferred to a separatory funnel as the flask was rinsed with water and methylene chloride. Additional ice water was added, and the solution was extracted with methylene chloride. The combined methylene chloride extracts were transferred to an Erlenmeyer flask and reduced in volume by one-half by boiling the steam bath. Nitrogen was bubbled through the solution to prevent bumping and decomposition. The resulting concentrated solution was then washed with de-aerated water and back extracted with methylene chloride several times. The methylene chloride extracts were dried, combined and again concentrated to a small volume (approximately 100 ml) by boiling on a steam bath under nitrogen. The

concentrated solution of 3-(3,4-diaminophenoxy)phenylacetylene was then used immediately in the end-capping reaction of benzil oligomer described below.

PREPARATION OF ACETYLENE TERMINATED QUINOXALINE (ATQ-O)

A methylene chloride solution containing 3-(3,4-diaminophenoxy) phenylacetylene was rapidly added to the m-cresol solution of benzil end-capped oligomer prepared above, and the flask was rinsed with methylene chloride. A distillation apparatus was then attached, and the flask was heated over an oil bath. The solution was stirred while heating to distill off the methylene chloride which had been added to begin the end-capping reaction. Once the methylene chloride was distilled, vacuum was applied and the temperature was raised sufficiently so that the m-cresol distilled rapidly from the flask. Distillation continued for 1/2 hour until the volume had been reduced to approximately 300 ml. At this point, the solution was tested for completeness of the end-capping reaction by removing of a 5-ml aliquot. Treatment with methanol yielded a small amount of yellow polymer which was purified. The purified polymer was filtered, dried, and dissolved in a small amount of methylene chloride. The infrared spectrum was then determined. The absence of carbonyl absorption at 1678 cm^{-1}, as well as the high intensity of the acetylene C-H absorption at 3300 cm^{-1}, were the determining factors in assessing the completeness of the end-capping reaction. If residual carbonyl absorption was detected, additional 3-(3,4-diaminophenoxy)phenylacetylene was prepared and added to the reaction mixture according to the above procedure.

When the end-capping reaction was completed, the m-cresol solution of ATQ-O polymer was added dropwise to 2 liters of stirred methanol, causing precipitation. The crude product was filtered, washed with several portions of methanol, and air dried. The dried polymer was then redissolved in methylene chloride, and the solution reduced to 1 liter. This solution was precipitated into methanol, and the methylene chloride was boiled away on the steam bath. The yellow polymer obtained was collected and reprecipitated from methylene chloride into methanol twice again, utilizing the same procedure. The purified ATQ-O polymer was then dried at 115°C in vacuo for 12 hours. The yield was 124 grams.

APPENDIX B

BATQ-H EXPERIMENTAL PROCEDURES

4-NITROBENZIL

Acetic anhydride (1760 ml) and benzoin (400 grams, 1.88 moles) were added to a 5-liter, three-neck, round-bottomed flask equipped with an overhead stirrer and a thermometer. The flask and its contents were cooled to $0^{\circ}C$ in a salt-ice bath. Concentrated sulfuric acid (400 ml) was then added slowly, with the solution temperature maintained at $0^{\circ}C$.

Adding the first 5 ml of sulfuric acid changed the solution from colorless to pale yellow as all the benzoin dissolved. Crystalline KNO_3 (220 grams) was pulverized and added slowly to the solution. The solution was then allowed to stand for 2 days at room temperature.

The solution was next poured into ice water and the liquid decanted. The thick, orange oil was repeatedly washed with water until the pH became neutral. Treating the oil with ether resulted in reprecipitation of white crystals. These crystals were collected by filtration and dried to give 190.7 grams of p-nitrobenzoin acetate, melting point $117^{\circ}C$ to $120^{\circ}C$, lit, m $127^{\circ}C$ to $128^{\circ}C$ (11), $124.5^{\circ}C$ to $125^{\circ}C$ (12). Treating the entire quantity of crude product with warm 70-percent nitric acid resulted in isolating, after workup, of 163 grams of p-nitrobenzil, m 134 to $137^{\circ}C$ lit, m $142^{\circ}C$ (11), $139.5^{\circ}C$ to $140^{\circ}C$ (12).

1,4-BIS(4-PHENYLGLYOXOYLPHENOXY)BENZENE

A 500-ml, three-neck, round-bottom flask was charged with 150 ml of dimethylsulfoxide (DMSO). A gas dispersion tube was then inserted into the liquid and dry nitrogen was bubbled through the DMSO for 15 minutes. Dry 4-nitrobenzil (15.0 grams, 0.0588 mole), hydroquinone (3.20 grams, 0.0291 mole) and potassium carbonate (10.0 grams, 0.073 mole) were added in that order to give a violet-colored reaction mixture. The mixture was stirred at room temperature for 2 days and heated over a water bath for 1 hour.

A solution consisting of 50 ml concentrated sulfuric acid in 1 liter of ice water was prepared. The reaction mixture was added to the solution. The mixture was filtered and the filtrate washed with water until the pH of the water was neutral. The pressed-dry filtrate was recrystallized from

ethyl acetate-ethanol to give 5.8 grams of 1,4-bis(4-phenylglyoxoylphenoxy)-benzene melting point 166°C, DSC.

APPENDIX C

PIQ EXPERIMENTAL PROCEDURES

PREPARATION OF 4,4'-BISBENZOIC ACID

a. **Coupling of 4-Chlorobenzoic Acid**

The 4-chlorobenzoic acid (402.2 grams) was dissolved in a solution of 350 grams of sodium hydroxide in 3500 ml water in a 12-liter flask. Pd/C catalyst (16 grams) was added, and the solution was heated to 75°C. Methanol (4 liters) was then added through a dropping funnel over a 6- to 7-hour period while the temperature was maintained between 70°C and 80°C. The flask was then cooled to room temperature and the insoluble crude product filtered. The acid salt product was redissolved in 8 liters of water and filtered through Celite to remove the catalyst. This filtered solution was acidified with hydrochloric acid to a pH of 1, forming a gelatinous precipitate. This precipitate was filtered, washed, and converted to a slurry by adding it to 2 liters of hot methanol. The slurry was again filtered and dried in a vacuum oven. DSC analysis showed no benzoic acid present in the filtered precipitate. Yields averaged 60 percent.

b. **Oxidation of 4,4'-Diacetylbiphenyl**

A slurry of 238.0 grams (1.00 mole) 4,4'-diacetylbiphenyl in 3 liters water was placed in a 12-liter, three-necked flask fitted with a motor-driven stirrer, reflux condenser thermometer, and dropper funnel. A solution of 123.3 grams (2.2 mole) potassium hydroxide in 500 ml of water was then added, and the mixture was then heated to gentle reflux. Potassium permanganate (948.0 grams, 6.0 mole) in 7.0 liters water was then added over a period of 2 hours. The mixture was stirred an additional 2 hours under reflux and allowed to cool. The acid salt solution filtered from the insoluble manganese dioxide. This solution was then acidified to pH 2 by carefully adding a 1:1 $H_2SO_4:H_2O$ solution. The cream-colored precipitate was filtered, washed with hot water, drained, and dried to give 232.3 grams of 4,4'-bisbenzoic acid.

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DIPHENYL SULFITE

Phenol (775 grams, 8.2 mole) and pyridine (6 grams, 8.1 mole) were added to a 5-liter, three-necked, round-bottomed flask equipped with an overhead stirrer, immersion thermometer, and dropping funnel. The flask was chilled to approximately 10°C and 1800 ml of anhydrous ethyl ether was added. The dropping funnel was charged with 300 ml of ethyl ether and 300 ml of thionyl chloride. The thionyl chloride solution was slowly added to the phenol-pyridine solution while flask temperature was maintained below 10°C by a water/ice bath. The solution was then stirred at room temperature for 1 hour and the solid pyridinium chloride precipitate filtered. The ethyl-ether solution was then washed with water, dried over magnesium sulfate, filtered, and the ether removed. The diphenylsulfite was used without additional purification for esterification.

DIPHENYL-4,4'-BISBENZOATE

A mixture of 900 ml of pyridine and 900 ml of dimethylformamide (DMF) was prepared is a 3-liter, three-necked flask equipped with a heating mantle, overhead stirrer, and immersion thermometer. The 4,4'-bisbenzoic acid (176 grams, 0.73 mole) was dissolved in the mixture, and the solution warmed to 90°C. Freshly prepared diphenyl sulfite (634 grams, 2.7 mole) was slowly added to the solution, which was then stirred overnight at 90°C. Reaction was noted by removing an aliquot of the solution, triturating it with water, isolating the precipitate, and verifying the solubility of the precipitate in chloroform.

Once the reaction was completed, the addition funnel was replaced with a distillation head and receiver. Half of the solvent was then removed under aspirator pressure. The remaining solution was allowed to cool to room temperature. The product was then separated by filtration and washed with methanol. The filtered ester product was then converted to a slurry by adding a warm 10-percent Na_2CO_3 solution. This slurry was recrystallized twice from toluene to give 187 grams (0.47 mole) of pure diphenyl-4,4'-bisbenzoate, a 64-percent yield based on diacid.

AF-R-553 PREPOLYMER SYNTHESIS

A 1-liter resin flask was equipped with a nitrogen inlet, overhead mechanical stirrer, distillation assembly, receiver and vacuum take-off. The flask was charged with sym-tris-(p-carbophenoxyphenyl)triazine (25.6 grams, 0.115 mole), diphenyl bisbenzoate (91.3 grams, 0.460 mole), AF-R-500 (116.5 grams, 0.560 mole) and redistilled m-cresol (150 ml). The assembly was then purged with nitrogen immersed in a 160°C oil bath under positive nitrogen pressure. The temperature of the oil bath was brought to 260°C and the contents stirred overnight. Water, m-cresol, and phenol were collected in the receiver during the synthesis. Reactants formed a clear viscous melt. The remaining m-cresol was then removed under a partial vacuum and the viscous prepolymer cooled to room temperature and broken up. Prepolymer yield was 200.8 grams, PMT, 183°C to 188°C.

PURIFICATION OF 3,3'-DIAMINOBENZIDINE

Crude 3,3'-diaminobenzidine (DAB) was recrystallized from a 1:1 volume ratio of ethylene glycol/water. This mixture was maintained under nitrogen. A large amount of charcoal was necessary to obtain colorless DAB. This procedure was followed by treating the filtered solution with sodium dithionite. Using this procedure, 15 pounds of nearly colorless DAB (melting point 182°C, DSC) were prepared.

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